

THEORETICAL STUDIES OF THE ELECTRONIC STATES OF LARGE
MOLECULES

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at the Australian National University.

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I wish to thank my supervisor, Professor D. P. Craig, for his guidance and encouragement throughout the course of this work. My thanks go to all of the scholars and fellows in the Theoretical and Physical Chemistry group for many stimulating and valuable discussions. I thank Professor R. S. Stein for several valuable discussions, and for his interest in this work. I also thank Professor J. H. Goldstein for his interest in this work.

I declare that the material presented in this thesis represents my own work, and that it has never been submitted for any other degree, in this or any other university.

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ABSTRACT

Two main problems are considered in this thesis. In the earlier chapters a new approach to Hückel calculations for pi electron problems has been developed. The approach, suggested by the exact theory of localized disturbances, relates the Hückel eigenfunctions and eigenvalues of a system under consideration to the known eigenfunctions and eigenvalues of a closely related system. The method is found to have a wide, but not general applicability. Relatively simple expressions are obtained, which are suitable for algebraic manipulation, and which greatly simplify computation. The treatment seems particularly well-adapted to following the effects, in the resulting molecular orbital quantities, of varying the heteroatom parameters. Application of the approach to the unsymmetrically substituted phosphonitrilic compounds gives insight into their pi electronic structure in the simple Hückel model. In particular, a comparison of the molecular orbital results with some of the known chemical reactions of the phosphonitriles, suggests a high correlation between the reactivity of various phosphorus sites, and the pi electron distribution in the in-plane pi system.

In the later chapters, the problem of the radiationless decay of excited electronic states of large molecules is considered. The theory of this phenomenon is reviewed. A treatment is devised to relate the rate of the radiationless decay

to basic properties of the electronic states. If the rate is regarded as a function of the energy gap between the zero vibrational levels of the initial and final electronic states, the Laplace transform of this function can be obtained as a simple expression. The quantities involved in this expression are the characteristic frequencies of the normal vibrations in the two states, the difference in molecular geometry between the two states, and the matrix element which couples the electronic wavefunctions. The internal conversions of benzene and deuterobenzene first singlet to ground state, are treated as numerical examples. The approximations involved in the model, and possible refinements of the treatment are discussed.

CHAPTER 1: INTRODUCTION

(i) The Scope of the Thesis

In principle, the behaviour of any large molecular system can be described in terms of the laws of quantum mechanics. In practice, however, these systems are so complex that the computation of accurate solutions to the Schrödinger equation is not feasible. Most of the theoretical treatments of large molecules therefore consist in the analysis of models, which attempt to reproduce many of the features of the molecule, in a greatly simplified system.

A model is usually generated as a series of simplifying assumptions about the behaviour of the system- for example, two quantities which are related in a very complex way in the real system may be empirically related by a simple function in the model. There is generally a fairly arbitrary compromise to be reached between the simplicity and solubility of the model, on the one hand, and its accuracy in simulating the complex physical situation of the real molecule, on the other.

The most useful models are those which constitute a reliable approximation to the physical system. The criterion for this is that the effects of the simplifying assumptions should combine, to give a value for the probable error in an observable quantity, small enough to put useful bounds on the quantity. Unfortunately, for models related to the properties of large molecules, there are many cases where this ideal can

not be obtained. In some cases the simplifying assumptions necessary to obtain a soluble model are too drastic to allow sufficiently narrow bounds; in others, it has not been possible to obtain a reasonable estimate of the probable error. In cases such as these the usefulness of a model is related to two main factors. In a useful model the simplifying assumptions are well-defined, and there is the possibility of examining them individually, and, often, of refining a simple model to take account of some of them. The other factor is the empirical success of the model. The simple Hückel treatment of pi electron problems is based on a series of extreme simplifying assumptions. It remains a useful model, nevertheless, because of its simplicity and its empirical success.

The two problems considered in this thesis are both concerned with the electronic states of large molecules. First, a ground state problem is considered. The Hückel molecular orbital treatment of pi electron systems is a comparatively old and well explored method. Its empirical success in the comparison of many properties of closely related series of conjugated carbon compounds is well known, as is its relative failure for more diverse systems^{1,2}. A different mathematical treatment of the same model has been found to give a simpler description, in many cases, while producing results identical with those of the more usual approach. Advantage is taken of this treatment to obtain a description of the pi electronic structures of the

phosphonitrilic compounds. In this way the application of the model to a very different series of closely related compounds can, to some extent, be empirically tested.

The second problem is concerned with the electronically excited states of large molecules. The radiationless decay of these states has been the subject of several recent theoretical treatments. A model is developed for the description of these processes, and some results obtained. The simplifying assumptions used in the model are examined in some detail.

In both cases the essential difference from other treatments is in a different mathematical approach. A simple result of the exact theory of localized perturbations is applied to the simple molecular orbital model, while an unusual use of the Laplace transformation, also exploited by Haarhof in his papers on the density of states^{3,4}, forms the basis for the solution of the model for radiationless transitions. The two treatments are related by the similarity of the mathematical methods used.

(ii) Green's Functions in Chemical Problems

In the exact quantum mechanical treatment of localized disturbances, Green's function methods may be used extensively in deriving the results. These methods have been applied in many recent theoretical treatments of widely differing chemical problems.

Green's functions are used for the solution of inhomogeneous differential equations, or for the solution of differential equations with inhomogeneous boundary conditions.

A homogeneous differential equation can be expressed in the form

$$\tilde{A}(\underline{q}) = 0 \quad (1)$$

where \tilde{A} is a linear differential operator, and \underline{q} is a generalized vector. Homogeneous boundary conditions are expressed

$\psi(\underline{q}^s) = 0$; $[\text{grad} \psi \cdot \underline{u}_n]_{\underline{q}^s} = 0$; or $[\text{grad} \psi \cdot \underline{u}_n]_{\underline{q}^s} + \lambda \psi(\underline{q}^s) = 0$ for all boundary points \underline{q}^s ; where λ is a scalar constant ;

\underline{u}_n is a unit vector normal to the surface at \underline{q}^s , and grad is a generalized vector gradient function given by $\underline{u}_i \frac{\partial}{\partial q_i}$.

The homogeneous differential equation with homogeneous boundary conditions is characterized by the property of solutions, that any scalar multiple of a solution is also a solution.

An inhomogeneous differential equation may be expressed

$$\tilde{A} \psi(\underline{q}) = \rho(\underline{q}) \quad (2)$$

In order to obtain the solution of this problem, a Green's function is defined as the solution $G(\underline{q}, \underline{q}')$ of

$$\tilde{A} G(\underline{q}, \underline{q}') = \delta(\underline{q} - \underline{q}') \quad (3)$$

and the function $\psi(\underline{q})$ may then be expressed in terms of the Green's function as a simple integral

$$\psi(\underline{q}) = \int G(\underline{q}, \underline{q}') \rho(\underline{q}') d\underline{q}' \quad (4)$$

For the problem of an inhomogeneous boundary condition, a

Green's function may be defined in an analogous way, and the solutions expressed as the surface integral over the boundary of a product involving the Green's function or its vector gradient.

The solution of equation (3) is usually simpler than the direct solution of (2), and, moreover, it enables the one general function G to be applied for the whole family of equations which could be generated by using different functions ρ . For many operators \check{A} of practical interest, however, it is not possible to obtain a solution for G in closed form. There are, however, several properties of the function G which make the approach useful even when the function cannot be given an algebraic form. One of these properties that has proved very useful in many chemical problems, is a relationship connecting G with the eigenfunctions of the operator \check{A} .

The eigenfunctions of A are the solutions, $\phi(q)$, of

$$\check{A} \phi(q) = \lambda \phi(q) \quad (5)$$

λ has a particular scalar value for each solution ϕ . A complete set of orthonormal solutions, ϕ_n , is considered. For simplicity it will be supposed that this set is countable. In this case, equation (3) can be expressed as an expansion in terms of the eigenfunctions

$$G(q, q') = \sum_n g_n(q') \phi_n(q) \quad (6)$$

$$\delta(q - q') = \sum_n d_n(q') \phi_n(q) \quad (7)$$

$$\check{A} \left[\sum_n g_n(q') \phi_n(q) \right] = \sum_n d_n(q') \phi_n(q) \quad (8)$$

Equation (7) is multiplied by $\phi_m^*(\underline{q})$, and integrated over all \underline{q} in the space.

$$\phi_m^*(\underline{q}') = \sum_n d_n(\underline{q}') \int \phi_m^*(\underline{q}) \phi_n(\underline{q}) d\underline{q}$$

or, since the ϕ_n form a complete, orthonormal set

$$\phi_m^*(\underline{q}') = d_m(\underline{q}') \quad (9)$$

Equation (8) may then be written

$$\check{A} \left[\sum_n g_n(\underline{q}') \phi_n(\underline{q}) \right] = \sum_n \phi_n^*(\underline{q}') \phi_n(\underline{q}) \quad (10)$$

As \check{A} is a linear operator, and $\check{A} \phi_n = \lambda_n \phi_n$

$$\sum_n g_n(\underline{q}') \lambda_n \phi_n(\underline{q}) = \sum_n \phi_n^*(\underline{q}') \phi_n(\underline{q}) \quad (10)$$

Coefficients of $\phi_n(\underline{q})$ are equated

$$g_n(\underline{q}') \phi_n(\underline{q}) = \phi_n^*(\underline{q}') \phi_n(\underline{q}) / \lambda_n$$

and substitution into equation (6) gives the result

$$G(\underline{q}, \underline{q}') = \sum_n \phi_n^*(\underline{q}') \phi_n(\underline{q}) / \lambda_n \quad (11)$$

Recent treatments of chemical problems which have used Green's function methods include many which are related to various properties of crystals. In isolated molecule problems relatively fewer applications have been found. Examples are the treatment of isotope effects in molecular vibrations by DeWames and Wolfram⁵, and some papers by Blinder^{6,7}, in which an approach is devised which gives the true energy eigenvalues of a system from a consideration of the time development of the non-stationary state defined by an approximate eigenfunction.

(iii) The Laplace Transformation

The Laplace transformation finds its main application as a method of solving differential equations with a single independent variable. The terms are multiplied through by a term $\exp(-px)$, where x is the independent variable and p is a dummy variable, and integrated from zero to infinity. In this way the differential equation can often be transformed into an algebraic equation, or a simpler differential equation, due to the relations

$$\int_0^{\infty} f'(x) e^{-px} dx = p \int_0^{\infty} f(x) e^{-px} dx - f(0) \quad (12)$$

and
$$\int_0^{\infty} \int_0^x f(y) dy \cdot e^{-px} dx = \frac{1}{p} \int_0^{\infty} f(x) e^{-px} dx \quad (13)$$

A problem sometimes arises in using this method, that a solution $f(x)$ for a problem is obtained in the form

$$g(p) = \int_0^{\infty} f(x) e^{-px} dx$$

The inverse transform is given by

$$f(x) = \int_{c-i\infty}^{c+i\infty} g(p) e^{px} dp$$

where, for sufficiently well-behaved f and g , c is an arbitrary real constant. Obtaining the inverse transform can present severe computational difficulties. The use of the Laplace transform in this manner has been fairly incidental in chemical problems, as most differential equations which are amenable to this treatment are relatively simple. There is, however, another type of problem in which the artificial introduction of the Laplace transformation has proved quite advantageous. This is exemplified in the papers by Haarhof on

the density of states^{3,4}, and the approach used in chapter 5 of this thesis.

If it is required to evaluate a sum of terms a_n , where the summation limit is such that the value of another function of n , e_n , is to be constrained by, for example, $0 \leq e_n \leq e$, the situation is very difficult to describe using the usual mathematical conventions. However, the sum may be described by

$$s(e) = \sum_n^{0 \leq e_n \leq e} a_n = \int_0^e \sum_n a_n \delta(e' - e_n) de'$$

Using equation (13) the Laplace transform $g(p)$ of the function $s(e)$ may be obtained in the form

$$g(p) = \frac{1}{p} \sum_n a_n \exp(-e_n p) \quad (14)$$

This has proved a useful result, since it has enabled the Laplace transforms of several very complex sums to be expressed in a simple algebraic form, and approximate inversion of the Laplace transform can give a simple smooth function approximating the complicated step function, $s(e)$.

(iv) Notation

The symbols used in the various mathematical treatments in this thesis are defined as they occur in the text. As far as possible the symbolism is kept consistent within each chapter, but many of the symbols represent different quantities in different chapters. The mathematical treatment in the various sections does not overlap greatly, and equations are numbered

independently in each chapter. References to equations from another chapter are specifically indicated as such. Some general conventions are used throughout the thesis. These are summarized here.

A tilde underscore is used to indicate a vector (e.g. \underline{r}). In most cases generalized vectors are discussed rather than three-dimensional vectors.

A breve is used to indicate an operator or a matrix (\check{A}).

Dirac's bra and ket notation is used for matrix elements. In the more straightforward cases matrix elements and vector components are indicated with the usual subscript notation.

Σ is used for summation, Π for product of terms. Where limits are not specified for these terms, infinite limits are implied. The same convention is used for integrals.

An asterisk denotes the complex conjugate of a quantity, a function, or an operator. A dagger denotes the hermitean conjugate of an operator.

$\delta(a-a')$, Dirac's delta function is used extensively. Where its arguments are vectors, its value is taken to be the product of delta functions of the components of the arguments. $\delta_{aa'}$, Kronecker's delta function is also used, with a distinguishing notation.

$d\tau$ is reserved for a general volume element. The notation $\int \dots d\tau$ is used for the integral over all space.

CHAPTER 2: A NOVEL TREATMENT OF SIMPLE π ELECTRON PROBLEMS(i) The Hückel Molecular Orbital Model

Much attention in theoretical chemistry has been concentrated on obtaining approximate solutions of the Schrödinger equation for isolated molecules, so as to obtain a picture of the molecular energy levels and electronic structures for various systems. Attention has focussed particularly on systems containing conjugated double bonds, since the properties of these compounds vary widely in a way that is difficult to explain without a detailed understanding of their electronic structures.

One of the earliest, and most widely used approximations has been the model originally proposed and explored by Hückel⁸⁻¹¹. As applied to the π electronic structures of systems containing conjugated double bonds, it consists in the following simplifications. Firstly, it is assumed that the nuclei, the inner electrons, and the electrons involved in sigma bonding have no role other than to provide a static "core" potential field for the π electrons. Then, it is further supposed that the interactions between the different π electrons have no effect other than to add a further shielding term to the core potential; any other effects are considered negligible. In this way the problem is reduced to that of finding the bound states of a single electron in the core field, and allotting the π electrons in turn to these

states in accordance with the Pauli exclusion principle. The lack of consideration of individual interactions between pi electrons eliminates singlet-triplet splittings, and so puts severe limitations on the use of the method for the treatment of excited states.

The one electron Schrödinger equation may be expressed

$$\hat{H}\psi_i = E_i\psi_i, \text{ where } \hat{H} = -\hbar^2/2m \cdot \nabla^2 + V^{\text{core}}$$

It is assumed that the one electron wavefunctions can be expressed as a linear combination of functions centred on the nuclei

$$\psi_i = \sum_x c_{ix} \phi_x$$

$$\text{Then } \sum_x c_{ix} \hat{H} \phi_x = E_i \sum_x c_{ix} \phi_x$$

$$\sum_x c_{ix} \int \phi_y^* \hat{H} \phi_x d\tau - E_i \sum_x c_{ix} \int \phi_y^* \phi_x d\tau = 0 \quad \text{for all } \phi_y.$$

In the simplest form of the Hückel treatment values are assigned to the integrals as follows:

$$\int \phi_x^* \hat{H} \phi_x d\tau = \alpha_x = \alpha + h_x \beta$$

$$\int \phi_x^* \hat{H} \phi_y d\tau = \beta_{xy} = k_{xy} \beta, \text{ if } \phi_x \text{ and } \phi_y \text{ are centred on adjacent nuclei,}$$

$$= 0 \quad \text{otherwise.}$$

$$\int \phi_x^* \phi_y d\tau = \delta_{xy}$$

The values of h_x and k_{xy} are assigned empirically: they are usually dependent only on the type of functions ϕ_x and ϕ_y , and on the type of nuclei on which they are centred. α and β are retained as parameters throughout this treatment. The scheme enables the c_{ix} to be determined completely, and the energies of the single electron bound states to be expressed

in terms of the two parameters α and β .

The approximations involved in this approach are quite drastic, but the resulting energies and wavefunctions obtained from calculations of this sort have provided good qualitative correlations with many physical and chemical properties, and provide a useful model of the pi electron structures of conjugated systems¹.

(ii) The Role of a Simpler Treatment

The main difficulty in applying this simple model to the calculation of electron distributions lies in the calculation itself. The main part of the calculation is a matrix diagonalization. Even for the relatively simple matrices which arise in a Hückel model this is a major task, usually necessitating the use of a digital computer. The disadvantage is particularly evident in studying series of closely related systems. Even though the matrices may differ only in the values of a few elements, a complete redetermination of eigenvalues and eigenvectors is usually required for each system studied. This makes the method particularly ill-adapted to studying, for example, the effect of choice of h_x or k_{xy} on the resulting electron distribution.

The use of a simple form of first and second order perturbation theory to produce approximations to the Hückel solutions has been explored as a means of overcoming this problem^{12,13}. The technique has been used in studying groups

of closely related systems¹⁴⁻¹⁷, and in following the effects of small changes in the choice of h_x or k_{xy}^1 . The main advantage of this approach lies in the simplicity of the calculations, and of the results, enabling various quantities to be expressed as simple functions of the parameters h and k . The disadvantage is that it is at best only an approximate method, and that its accuracy decreases drastically with increasing perturbation.

It can thus be seen that there is a place for a treatment which will provide results identical with those from the matrix diagonalization, while retaining much of the numerical simplicity of the perturbation techniques. Such an approach is explored through the remainder of this chapter.

(iii) Treatment of a Large Localized Disturbance*

In 1954 Lax¹⁸ set down an approach to deal generally with a large, localized disturbance in a quantum mechanical system, expressing the results in terms of the known, or obtainable, eigenfunctions of a corresponding undisturbed

* Throughout this chapter "disturbance" is used rather than the more usual "large perturbation". This is to emphasize the distinction of the exact method described, from the approximate methods derived from perturbation theory and, in particular, to avoid confusion where the latter methods enter the discussion.

system. He noted the wide applicability of the result, and suggested its application to the problem of lattice vibrations in a crystal containing an impurity site. Slater and Koster¹⁹ derived essentially the same result using a different approach, and applied it in a detailed consideration of impurity levels in crystal electronic spectra*. The same approach was used by Craig and Philpott²⁰⁻²² in their studies of mixed crystal electronic spectra. These authors noted the close analogy between simple molecular orbital models and the crystal models used.

It has been found that the approach has a widespread, though not general applicability in molecular orbital calculations, and provides an alternative means of computing the exact Hückel eigenfunctions for a wide range of systems of practical interest.

The result obtained by Lax was derived initially from a matrix approach. The eigenfunctions, ϕ_p and eigenvalues, E_p of an hermitean operator, \tilde{H} are known.

$$\sum_{j=1}^N H_{ij} \phi_{jp} = E_p \phi_{ip} \quad (1)$$

For convenience the eigenfunctions ϕ_p are normalized. It is required to find the eigenfunctions of a locally disturbed operator, $\tilde{H} + \tilde{h}$

$$\sum_{j=1}^N (H_{ij} + h_{ij}) \psi_j = \epsilon \psi_i \quad (2)$$

* A closely analogous approach was used by Lifshitz in several papers between 1943 and 1952 (references 23-31). Many Western workers appear to have been unaware of these results.

The condition that h_{rs} is a localized disturbance may be imposed by the condition $h_{rs} \equiv 0$ unless $r, s \leq k < N$. Expressed in matrix notation equation (2) becomes

$$(\check{H} + \check{h}) \check{\psi} = \epsilon \check{\psi} \quad (2a)$$

which rearranges to $\check{\psi} = (\epsilon - \check{H})^{-1} \check{h} \check{\psi}$, or

$$\psi_i = \sum_{r=1}^k \sum_{s=1}^k (\epsilon - H)^{-1}_{ir} h_{rs} \psi_s \quad (3)$$

The matrix $\check{\phi}$ with elements ϕ_{jp} is now considered. As \check{H} is hermitean, and $\check{\phi}$ is unitary, $\check{\phi}^{-1} \equiv \check{\phi}^\dagger$.

From equation (1) $\check{H}^{-1} = \check{\phi} E^{-1} \check{\phi}^\dagger$

$$\begin{aligned} (\epsilon - \check{H})^{-1} &= \check{\phi} \check{\phi}^\dagger (\epsilon - E)^{-1} \\ (\epsilon - H)^{-1}_{ir} &= \sum_{p=1}^N \frac{\phi_{ip} \phi_{rp}^*}{\epsilon - E_p} \end{aligned} \quad (4)$$

Substituting into (3)

$$\psi_i = \sum_{r=1}^k \sum_{s=1}^k \sum_{p=1}^N \frac{\phi_{ip} \phi_{rp}^*}{\epsilon - E_p} h_{rs} \psi_s \quad (5)$$

Koster and Slater obtain a similar result using a simple Green's function technique. If the complete set of solutions $\phi_{n,k}(\underline{r})$ is known for the differential equation $(\check{H}_0 - E) \phi(\underline{r}) = 0$ then the Green's function for the problem can be expanded in terms of the solutions ϕ . The Green's function is defined as the solution, $G(\underline{r}, \underline{r}')$, of

$$(\check{H}_0 - E) G(\underline{r}, \underline{r}') = \delta(\underline{r} - \underline{r}') \quad (6)$$

and is given, in this case, by

$$G(\underline{r}, \underline{r}') = \sum_{n,k} \frac{\phi_{n,k}(\underline{r}') \phi_{n,k}(\underline{r})}{E_n(k) - E} \quad (7)$$

If the equation $(H_0 + H_1 - E) \psi = 0$ is now considered, it can be expressed

$$(\check{H}_0 - E)\check{\psi} = H_1 \check{\psi} \quad (8)$$

The solution is given by the integral

$$\check{\psi}(\underline{r}') = \int \check{\psi}(\underline{r}) \check{H}_1 G(\underline{r}, \underline{r}') d\tau = \int \check{\psi}(\underline{r}) H_1 \left[\sum_{n,k} \frac{\phi_{n,k}^*(\underline{r}') \phi_{n,k}(\underline{r})}{E_n(k) - E} \right] d\tau \quad (9)$$

This is the same result as (5) in an integral form. Equation (5) could be obtained by expanding $\check{\psi}$ in equation (9) in terms of basis functions.

(iv) Application to a System Containing a Single Heteroatomic Site

The application of equation (5) in Hückel molecular orbital calculations is most useful in dealing with a disturbance which affects only one element of the H matrix. As \check{H} is hermitean, this must be a diagonal element, and will, for convenience, be chosen as the element H_{11} .

If the solutions $\check{\psi}$ and E of the Hückel single pi electron equation are known for one system, then for another system whose secular equation differs only in one element of the H matrix, the solutions $\check{\psi}$ and ϵ are defined by $(\check{H} + \check{h})\check{\psi} = \epsilon \check{\psi}$, where h_{11} is the only non-zero element of \check{h} . Application of equation (5) in this case leads to a very simple result

$$\check{\psi}_i = h_{11} \check{\psi}_1 \sum_p \phi_{ip}^* \phi_{1p} / (\epsilon - E_p) \quad (10)$$

If $i=1$, this becomes

$$\check{\psi}_1 = h_{11} \sum_p \phi_{1p}^* \phi_{1p} / (\epsilon - E_p) \quad (11)$$

Equation (11) may be solved for ϵ . Substitution for ϵ in

equation (10), with the normalization condition, solves for $\check{\psi}$.

The eigenvalues, ϵ , are still the roots of the same degree p polynomial equation as would arise from a complete matrix diagonalization. The form of equation (11) is, however, more convenient than expressing the same equation as the eigenvalues of a large matrix. It is in a particularly suitable form for numerical evaluation, as terms with E_p close to ϵ will tend to dominate the summation, enabling the use of rapidly converging iterative techniques.

The first order perturbation treatment of Hückel molecular orbital problems is based on the relation¹²

$$\frac{\partial E_p}{\partial H_{yy}} = \phi_{yp}^* \phi_{yp} \quad (12)$$

For small changes in H_{yy} , $\delta E_p = \delta H_{yy} \cdot \frac{\partial E_p}{\partial H_{yy}}$; hence, for small h

$$\epsilon_1 \approx h_{yy} \frac{\phi_{yp}^* \phi_{yp}}{\epsilon_p - E_p} \quad (13)$$

It is apparent, then, that the perturbation theory treatment is equivalent to taking only the largest term of the sum in (11). This will be a better approximation for small h_{yy} , and widely spaced E_p . It will also be a better approximation for intermediate values of ϵ , as contributions from the smaller terms in the sum will tend to cancel in this region.

The use of equation (11) is considered in detail for a simple example. For simplicity the matrix of h_x and k_{xy} is used instead of the H matrix. The eigenvalues, e , are then related to the one electron energy eigenvalues by the relation $\epsilon = \alpha + e\beta$. The pyridine molecule is considered as a disturbed benzene molecule. The properties of carbon-nitrogen bonds in

conjugated systems are very similar to those of carbon-carbon bonds, and it has been usual to assign a bond parameter k_{CN} not greatly differing from 1 in Hückel calculations¹ ($k_{CC}=1$, $h_C=0$, in the usual convention). The only disturbance, then, is in the h_N matrix element. The eigenvalues and eigenvectors of the benzene molecule are shown in table 2-1. The choice of real coefficients for the degenerate states is for convenience only; the same results are obtained if complex values are used. Direct substitution in equation (11) gives the following equation for the pyridine system.

$$1 = h_N \left(\frac{1}{6(e-2)} + \frac{1}{3(e-1)} + \frac{1}{3(e+1)} + \frac{1}{6(e+2)} \right) \quad (14)$$

Because of the degeneracy of the benzene states this equation is of the fourth rather than the sixth degree in e . The other two values of e are readily found from symmetry considerations. The plane intersecting N_1 and C_4 in pyridine is a symmetry plane, as is the plane intersecting C_1 and C_4 in benzene. States which are antisymmetric with respect to reflection in this plane must have nodes at atoms 1 and 4. Since the N atom carries no electron density in these pyridine states, they will be identical with the corresponding benzene states. The other four states are given by the solutions of (14) for e , and by substitution in (10). Equation (14) is simply solved numerically by equating the most sensitive term in e to the remainder of the expression. An approximation to e , substituted in the right hand side gives a much better approximation in the left. Successive iterations oscillate

Table 2-1: Hückel Molecular Orbitals for Benzene

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
Energy	2	1	1	-1	-1	-2
Coefficients						
χ_1	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}$	0	$\frac{1}{\sqrt{3}}$	0	$\frac{1}{\sqrt{6}}$
χ_2	$\frac{1}{\sqrt{6}}$	$\frac{1}{2\sqrt{3}}$	$\frac{1}{2}$	$\frac{-1}{2\sqrt{3}}$	$\frac{1}{2}$	$\frac{-1}{\sqrt{6}}$
χ_3	$\frac{1}{\sqrt{6}}$	$\frac{-1}{2\sqrt{3}}$	$\frac{1}{2}$	$\frac{-1}{2\sqrt{3}}$	$-\frac{1}{2}$	$\frac{1}{\sqrt{6}}$
χ_4	$\frac{1}{\sqrt{6}}$	$\frac{-1}{\sqrt{3}}$	0	$\frac{1}{\sqrt{3}}$	0	$\frac{-1}{\sqrt{6}}$
χ_5	$\frac{1}{\sqrt{6}}$	$\frac{-1}{2\sqrt{3}}$	$-\frac{1}{2}$	$\frac{-1}{2\sqrt{3}}$	$\frac{1}{2}$	$\frac{1}{\sqrt{6}}$
χ_6	$\frac{1}{\sqrt{6}}$	$\frac{-1}{2\sqrt{3}}$	$-\frac{1}{2}$	$\frac{-1}{2\sqrt{3}}$	$-\frac{1}{2}$	$\frac{-1}{\sqrt{6}}$

about the correct value, and converge rapidly. Details of the iteration results for $h_N = 0.5$ and for $h_N = 1.0$ are provided in table 2-2. Values of the eigenvectors and eigenvalues for the pyridine molecule with $h_N = 0.5$ and $h_N = 1.0$ are shown in table 2-3. They are in complete agreement with those given by Coulson and Streitwieser³², obtained by matrix diagonalization.

Table 2-2: Iterative Solutions for Pyridine

	e_1	e_2	e_4	e_6
$h_N = 1.0$; Iteration results.				
	2.3243243	1.3529412	-0.6842105	-1.8878505
	2.2734542	1.3126363	-0.7058845	-1.8913327
	2.2789797	1.3180588	-0.7045462	-1.8912161
	2.2783494	1.3173480	-0.7046292	-1.8912200
	2.2784209	1.3174415	-0.7046241	-1.8912198
	2.2784128	1.3174292	-0.7046244	
	2.2784137	1.3174308		
	2.2784136	1.3174306		
$h_N = 0.5$; Iteration results.				
	2.1100917	1.1714286	-0.8378378	-1.9329609
	2.1073886	1.1670770	-0.8410194	-1.9336865
	2.1074476	1.1671970	-0.8409608	-1.9336782
	2.1074464	1.1671937	-0.8409619	-1.9336783
	2.1074464	1.1671937	-0.8409618	

Table 2-3: Hückel Molecular Orbitals for Pyridine

	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6
$h_N = 1.0$						
Energy	2.2784136	1.3174306	1	-0.7046244	-1	-1.8912198
Coeff.						
1	0.6462760	0.5168762	0	0.4964503	0	0.2621134
2	0.4131040	0.0820362	$\frac{1}{2}$	-0.4231307	$\frac{1}{2}$	-0.3789137
3	0.2949458	-0.4087993	$\frac{1}{2}$	-0.1983022	$-\frac{1}{2}$	0.4544958
4	0.2589045	-0.6206008	0	0.5628592	0	-0.4806377
$h_N = 0.5$						
Energy	2.1074464	1.1671937	1	-0.8409618	-1	-1.9336783
Coeff.						
1	0.5207063	0.5713738	0	0.5459130	0	0.3230728
2	0.4185037	0.1906085	$\frac{1}{2}$	-0.3660242	$\frac{1}{2}$	-0.3931276
3	0.3612678	-0.3488967	$\frac{1}{2}$	-0.2381006	$-\frac{1}{2}$	0.4371095
4	0.3428489	-0.5978386	0	0.5662577	0	-0.4521016

(v) The Use of Symmetry to Extend the Range of Applicability

In certain circumstances equation (11) can be applied to disturbances other than strictly local disturbances. If a series of identical disturbances occurs at a set of symmetrically related sites, the use of appropriate symmetry orbitals in the basis set enables all of the disturbances to be expressed in the variation of a single matrix element. Moreover, when symmetry orbitals are used in this way, the system which is chosen as the "corresponding undisturbed" system need not necessarily be based on similar symmetry orbitals, but may use a basis of atomic orbitals, or even of symmetry orbitals of a different type. The only restriction is that it should be possible to express the known undisturbed system and the required disturbed system in terms of any convenient basis set by matrices which differ only in one element. A series of examples is presented to demonstrate the versatility the approach acquires with the use of symmetry orbitals.

Example: The three diazines referred to benzene.

If real coefficients are chosen for the degenerate states in the benzene model (as in table 2-1), the eigenfunctions have two perpendicular symmetry planes. Each of the diazines can be aligned so as to retain at least one of these symmetry planes for its eigenfunctions. This is shown in figure 2-1. In order to find the eigenfunctions of pyrimidine, for example, the states which are symmetric with

FIGURE 2-1: Symmetry Planes of the Diazines

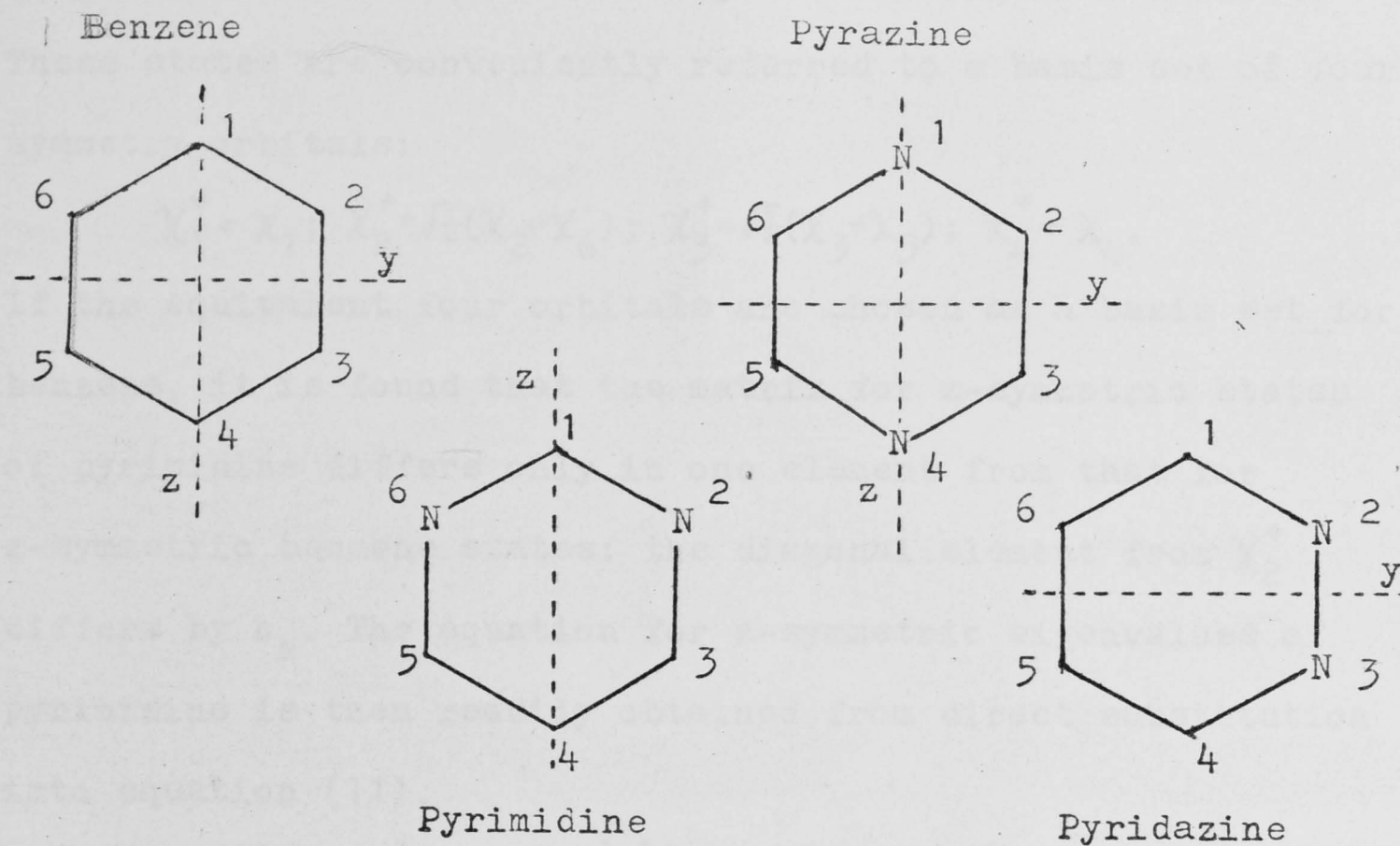
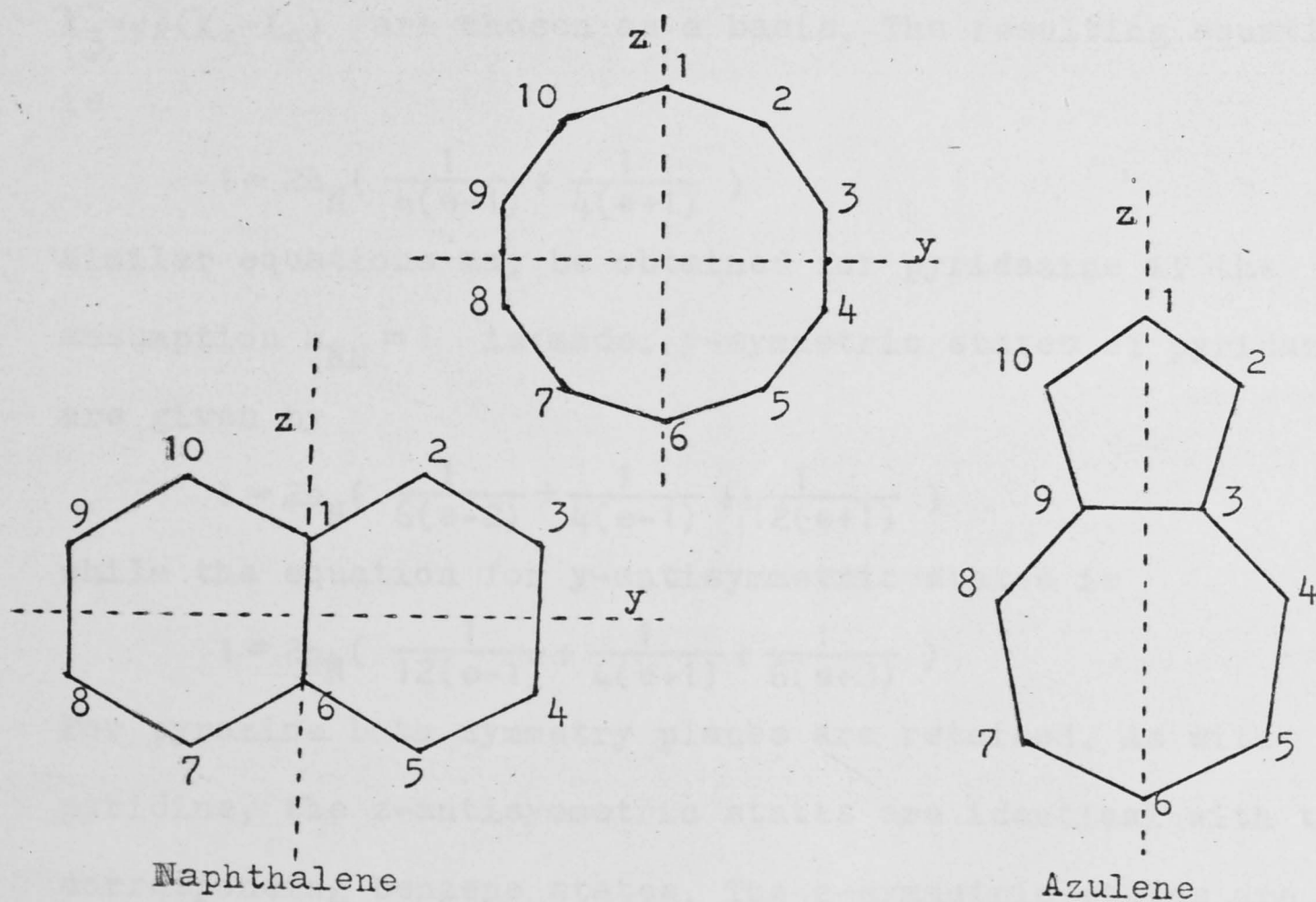


FIGURE 2-2: Naphthalene and Azulene as Disturbed Cyclic Polyenes



respect to reflection in the z plane are considered first. These states are conveniently referred to a basis set of four symmetry orbitals:

$$\chi_1^+ = \chi_1; \chi_2^+ = \sqrt{\frac{1}{2}}(\chi_2 + \chi_6); \chi_3^+ = \sqrt{\frac{1}{2}}(\chi_3 + \chi_5); \chi_4^+ = \chi_4.$$

If the equivalent four orbitals are chosen as a basis set for benzene, it is found that the matrix for z -symmetric states of pyrimidine differs only in one element from that for z -symmetric benzene states: the diagonal element from χ_2^+ differs by h_N . The equation for z -symmetric eigenvalues of pyrimidine is then readily obtained from direct substitution into equation (11).

$$1 = 2h_N \left(\frac{1}{6(e-2)} + \frac{1}{12(e-1)} + \frac{1}{12(e+1)} + \frac{1}{6(e+2)} \right)$$

For z -antisymmetric states of pyrimidine a similar treatment is obtained when the symmetry orbitals $\chi_2^- = \sqrt{\frac{1}{2}}(\chi_2 - \chi_6)$ and $\chi_3^- = \sqrt{\frac{1}{2}}(\chi_3 - \chi_5)$ are chosen as a basis. The resulting equation is

$$1 = 2h_N \left(\frac{1}{4(e-1)} + \frac{1}{4(e+1)} \right)$$

Similar equations may be obtained for pyridazine if the assumption $k_{NN} = 1$ is made. y -symmetric states of pyridazine are given by

$$1 = 2h_N \left(\frac{1}{6(e-2)} + \frac{1}{4(e-1)} + \frac{1}{12(e+1)} \right)$$

while the equation for y -antisymmetric states is

$$1 = 2h_N \left(\frac{1}{12(e-1)} + \frac{1}{4(e+1)} + \frac{1}{6(e+2)} \right)$$

For pyrazine both symmetry planes are retained. As with pyridine, the z -antisymmetric states are identical with the corresponding benzene states. The z -symmetric states are

given by

$$1 = 2h_N \left(\frac{1}{6(e-2)} + \frac{1}{3(e+1)} \right) \quad \text{z-symmetric, y-symmetric.}$$

$$1 = 2h_N \left(\frac{1}{3(e-1)} + \frac{1}{6(e+2)} \right) \quad \text{z-symmetric, y-antisymmetric.}$$

The eigenvectors in these cases are provided by a series of similar equations, readily derived by substitution in (10).

Example: Naphthalene and azulene referred to "planar cyclodecapentaene".

It is not possible by direct application of equation (11) to describe a system where the disturbance consists of a difference in the bond parameter, k . This is because of the hermitean property of the Hückel \hat{H} operator, which requires that any off-diagonal disturbance be reflected in at least two matrix elements. However, for a bond which is symmetrically disposed in the system, it is possible to cause the disturbance to appear only in a diagonal element by choosing appropriate symmetry orbitals as the basis set. The naphthalene and azulene systems are here considered as derivatives of the ten-membered cyclic polyene, with the "disturbance" consisting in the presence of a symmetrically disposed bridging bond.

The eigenfunctions of cyclic polyenes are given by well known formulae^{32,33}. With the choice of real coefficients for the degenerate levels, and a z symmetry plane passing through the atomic sites 1 and 6, the states of the ten membered ring may be expressed:

z-symmetric states:

$$e_1 = 2 ; \quad c_{1m} = \frac{1}{\sqrt{10}} .$$

$$e_2 = 2 \cos \frac{\pi}{5} ; \quad c_{2m} = \frac{1}{\sqrt{5}} \cdot \cos (m-1) \frac{\pi}{5} .$$

$$e_4 = 2 \cos \frac{2\pi}{5} ; \quad c_{4m} = \frac{1}{\sqrt{5}} \cdot \cos (m-1) \frac{2\pi}{5} .$$

$$e_6 = 2 \cos \frac{3\pi}{5} ; \quad c_{6m} = \frac{1}{\sqrt{5}} \cdot \cos (m-1) \frac{3\pi}{5} .$$

$$e_8 = 2 \cos \frac{4\pi}{5} ; \quad c_{8m} = \frac{1}{\sqrt{5}} \cdot \cos (m-1) \frac{4\pi}{5} .$$

$$e_{10} = -2 ; \quad c_{10m} = \frac{(-1)^{m-1}}{\sqrt{10}} .$$

z-antisymmetric states:

$$e_3 = 2 \cos \frac{\pi}{5} ; \quad c_{3m} = \frac{1}{\sqrt{5}} \cdot \sin (m-1) \frac{\pi}{5} .$$

$$e_5 = 2 \cos \frac{2\pi}{5} ; \quad c_{5m} = \frac{1}{\sqrt{5}} \cdot \sin (m-1) \frac{2\pi}{5} .$$

$$e_7 = 2 \cos \frac{3\pi}{5} ; \quad c_{7m} = \frac{1}{\sqrt{5}} \cdot \sin (m-1) \frac{3\pi}{5} .$$

$$e_9 = 2 \cos \frac{4\pi}{5} ; \quad c_{9m} = \frac{1}{\sqrt{5}} \cdot \sin (m-1) \frac{4\pi}{5} .$$

In the case of azulene, symmetry orbitals symmetric or antisymmetric with respect to reflection in the z plane are chosen as a basis. For the symmetric states the disturbance is +1 in the diagonal matrix element of the orbital

$\frac{1}{\sqrt{2}} (\chi_3 + \chi_9)$, due to the bonding interaction, $+\beta$, between χ_3 and χ_9 in azulene. In the antisymmetric states a disturbance of -1 occurs in the diagonal matrix element of the orbital $\frac{1}{\sqrt{2}} (\chi_3 - \chi_9)$. The equations for the eigenvalues of azulene

are thus:

z-symmetric states.

$$1 = \frac{1}{10(e-2)} + \frac{\cos^2 2\pi/5}{5(e-2 \cos \pi/5)} + \frac{\cos^2 4\pi/5}{5(e-2 \cos 2\pi/5)} + \frac{\cos^2 6\pi/5}{5(e-2 \cos 3\pi/5)} \\ + \frac{\cos^2 8\pi/5}{5(e-2 \cos 4\pi/5)} + \frac{1}{10(e+2)} \quad .$$

z-antisymmetric states.

$$-1 = \frac{\sin^2 2\pi/5}{5(e-2 \cos \pi/5)} + \frac{\sin^2 4\pi/5}{5(e-2 \cos 2\pi/5)} + \frac{\sin^2 6\pi/5}{5(e-2 \cos 3\pi/5)} \\ + \frac{\sin^2 8\pi/5}{5(e-2 \cos 4\pi/5)} \quad .$$

For naphthalene, the disturbance occurs in the z plane. States which are antisymmetric about z are therefore not affected, as z is a nodal plane for these states. The states symmetric about the z plane are described in terms of symmetry orbitals based on the perpendicular y symmetry plane. In this way the disturbance due to the bridging bond appears as +1 in the diagonal matrix element of the orbital $\sqrt{2}(\chi_1 + \chi_6)$, and as -1 in the element from the orbital $\sqrt{2}(\chi_1 - \chi_6)$. The equations obtained are:

$$1 = \frac{1}{10(e-2)} + \frac{1}{5(e-2 \cos \pi/5)} + \frac{1}{5(e-2 \cos 2\pi/5)} \quad : \text{ z-symm., y-symm.} \\ -1 = \frac{1}{5(e-2 \cos 3\pi/5)} + \frac{1}{5(e-2 \cos 4\pi/5)} + \frac{1}{10(e+2)} \quad : \text{ z-symm.,} \\ \text{ y-antisymm.}$$

Example: Biphenyl referred to benzene.

As previously pointed out, the basis sets of the disturbed and reference systems need not be equivalent, provided that

the \check{H} matrices differ in only one element. Thus, the states of the biphenyl system may be classified in terms of symmetry about the y plane, which intersects the 1-1' bond. Both sets of states can then be described in a symmetry orbital basis by interaction matrices which differ in only one element from the matrix for benzene in an atomic orbital basis. The y-symmetric states have a disturbance of +1 in the diagonal element from $\chi_1^+ = \sqrt{\frac{1}{2}}(\chi_1 + \chi_{1'})$, while y-antisymmetric states have a disturbance -1 in the diagonal element from $\chi_1^- = \sqrt{\frac{1}{2}}(\chi_1 - \chi_{1'})$. The equations which arise from (11) are in this case:

$$1 = \frac{1}{6(e-2)} + \frac{1}{3(e-1)} + \frac{1}{3(e+1)} + \frac{1}{6(e+2)} \quad \text{for y-symmetric states.}$$

$$-1 = \frac{1}{6(e-2)} + \frac{1}{3(e-1)} + \frac{1}{3(e+1)} + \frac{1}{6(e+2)} \quad \text{for y-antisymmetric states.}$$

The four states which are antisymmetric about the z plane (long axis) will consist of two sets of doubly degenerate states, each identical with the corresponding benzene z-antisymmetric state.

(vi) Disturbances Involving More than One Matrix Element

The use of the general result expressed in equation (5) for systems other than those which can be covered by the special case where equations (10) and (11) apply, is restricted by the complexity of the sums that arise. There is, however, at least one other special case where equation (5) reduces to a simple form, suitable as an alternative to

matrix diagonalization. The simplest case of a disturbance which affects more than one matrix element, is that of a disturbance which affects only a single pair of off-diagonal matrix elements: $h_{11} = h_{22} = 0$; $h_{12} = h_{21}^* \neq 0$. In this case equation (5) reduces to

$$\psi_i = \sum_p \frac{\phi_{ip} (\phi_{1p}^* h_{12} \psi_2 + \phi_{2p}^* h_{12}^* \psi_1)}{\epsilon - E_p} \quad (15)$$

This equation is most useful when a system is related to an "undisturbed" system consisting of two non-interacting parts, the "disturbed" system containing a bridging bond. In this case the eigenfunctions, ϕ , of the undisturbed system are not coupled, but have components over one part of the system only. If the two non-interacting sets of basis orbitals are designated χ_j (includes χ_1) and χ_k (includes χ_2), and the sets of states ϕ_q and ϕ_r provide components only over χ_j or χ_k , respectively, then

$$\psi_j = \sum_q \frac{\phi_{jq} \phi_{1q}^* h_{12} \psi_2}{\epsilon - E_q} ; \quad \psi_k = \sum_r \frac{\phi_{kr} \phi_{2r}^* h_{12}^* \psi_1}{\epsilon - E_r} \quad (16)$$

$$1 = h_{12}^* h_{12} \sum_q \frac{\phi_{1q}^* \phi_{1q}}{\epsilon - E_q} \cdot \sum_r \frac{\phi_{2r}^* \phi_{2r}}{\epsilon - E_r} \quad (17)$$

Expression (17), while rather more complex than (11), is still in a convenient form for numerical solution. It can be further simplified in several cases of interest. Where a single site is added to a system one of the discrete parts of the undisturbed system is a single atomic orbital. Equation (17) simplifies in this case to a simple sum, very similar

to (11). The form is

$$1 = \frac{h_{12}^* h_{12}}{\epsilon - H_{11}} \sum_r \frac{\phi_{2r}^* \phi_{2r}}{\epsilon - E_r} \quad (18)$$

This result may be directly applied, for example, to finding the Hückel eigenfunctions of aniline, or of the benzyl radical from those of benzene as an undisturbed system, while, with the use of symmetry orbitals, quinodimethane, phenylenediamine, diphenylamine, or even anthracene eigenfunctions may be obtained from benzene eigenfunctions.

Two other cases where a simple result is obtained are those resulting from addition of a vinyl or a phenyl group to a known system. The equations derived are, for the vinyl case

$$1 = h_{12}^* h_{12} \frac{\alpha - \epsilon}{(\alpha - \epsilon)^2 - \beta^2} \sum_r \frac{\phi_{2r}^* \phi_{2r}}{\epsilon - E_r} \quad (19)$$

For the phenyl case there are always two states localized on the benzene ring with eigenvalues $\pm\beta$. The other states are described by an equation which reduces to

$$(\epsilon - \alpha) - \frac{2\beta^2}{(\epsilon - \alpha)} - \frac{2\beta^4}{(\epsilon - \alpha)^2 - 3\beta^2} = h_{12}^* h_{12} \sum_r \frac{\phi_{2r}^* \phi_{2r}}{\epsilon - E_r} \quad (20)$$

For more complex disturbances it seems unlikely that equations can be obtained from this method which would offer a distinct advantage over direct matrix diagonalization. However the range of applicability of equations (11) and (17) is quite extensive, and it seems that most systems of practical interest could be solved by these methods with reference to systems with known Hückel molecular orbitals.

(vii) Systems which may be Referred to the Benzene System

In this section a table of the various systems which may conveniently be related by these methods to benzene as an "undisturbed" model system is presented. Numerical solutions for most of these systems are available in accessible tables^{32,34}, and are not presented here. Instead, the equations obtained for the eigenvalues and eigenvectors are given. These are of particular interest in systems which contain heteroatoms, where a parameter is fairly arbitrary, or in hydrocarbon systems such as azulene or the polyphenyls, where there may be reason for the assignment of a bond parameter k_{CC} other than 1. In these cases the variation of the eigenfunctions with changing parameter value can be followed with the use of the equations given. In other cases the disturbance is expressed in the Hückel model by a definite fixed change in the matrix element. The equations are of less interest here, although they do provide insight into the relationships between the molecular orbital structures of various systems. The extent of the table is a good indication of the scope of the method.

The numbering and symmetry axes of benzene and of the diazines are taken from figure 2-1. Numbering and symmetry axes for other systems are shown in figures 2-3, 2-4, and 2-5, except for the amino- and vinylbenzenes, where numbering and axis conventions parallel those used for the azines.

Group (a) : Systems derived from equations (11) and (10).

Pyridine: eigenvalues

$$\frac{6}{h_N} = \frac{1}{e-2} + \frac{2}{e-1} + \frac{2}{e+1} + \frac{1}{e+2}$$

eigenfunctions

$$\frac{\psi_2}{\psi_1} = \frac{\psi_6}{\psi_1} = \frac{h_N}{6} \left(\frac{1}{e-2} + \frac{1}{e-1} - \frac{1}{e+1} - \frac{1}{e+2} \right)$$

$$\frac{\psi_3}{\psi_1} = \frac{\psi_5}{\psi_1} = \frac{h_N}{6} \left(\frac{1}{e-2} - \frac{1}{e-1} - \frac{1}{e+1} + \frac{1}{e+2} \right)$$

$$\frac{\psi_4}{\psi_1} = \frac{h_N}{6} \left(\frac{1}{e-2} - \frac{2}{e-1} + \frac{2}{e+1} - \frac{1}{e+2} \right)$$

There are two states identical with benzene
z-antisymmetric states.

Pentadienyl: Eigenvalues can be obtained from the pyridine
equation with $h_N = -\infty$

Pyrimidine: z-symmetric states

$$\frac{6}{h_N} = \frac{2}{e-2} + \frac{1}{e-1} + \frac{1}{e+1} + \frac{2}{e+2}$$

$$\frac{\psi_1}{\psi_2} = \frac{h_N}{3} \left(\frac{1}{e-2} + \frac{1}{e-1} - \frac{1}{e+1} - \frac{1}{e+2} \right)$$

$$\frac{\psi_3}{\psi_2} = \frac{h_N}{6} \left(\frac{2}{e-2} - \frac{1}{e-1} + \frac{1}{e+1} - \frac{2}{e+2} \right)$$

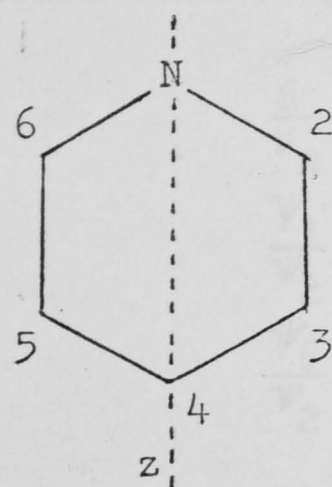
$$\frac{\psi_4}{\psi_2} = \frac{h_N}{3} \left(\frac{1}{e-2} - \frac{1}{e-1} - \frac{1}{e+1} + \frac{1}{e+2} \right)$$

z-antisymmetric states

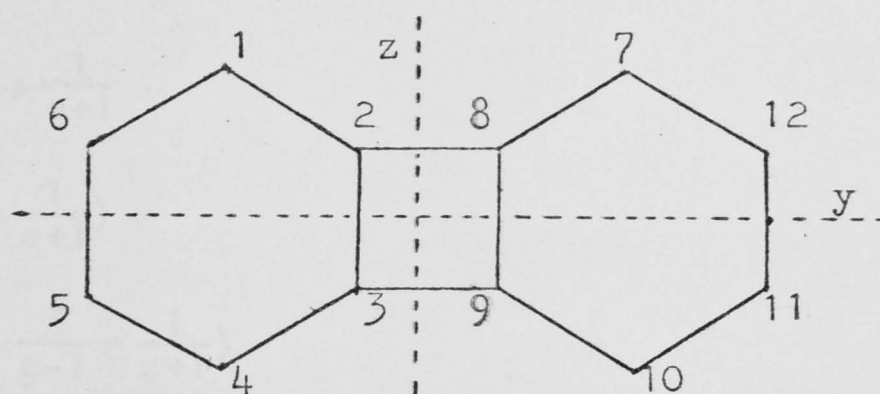
$$\frac{2}{h_N} = \frac{1}{e-1} + \frac{1}{e+1}$$

$$\frac{\psi_3}{\psi_2} = \frac{h_N}{2} \left(\frac{1}{e-1} - \frac{1}{e+1} \right) ; \quad \psi_1 = \psi_4 = 0$$

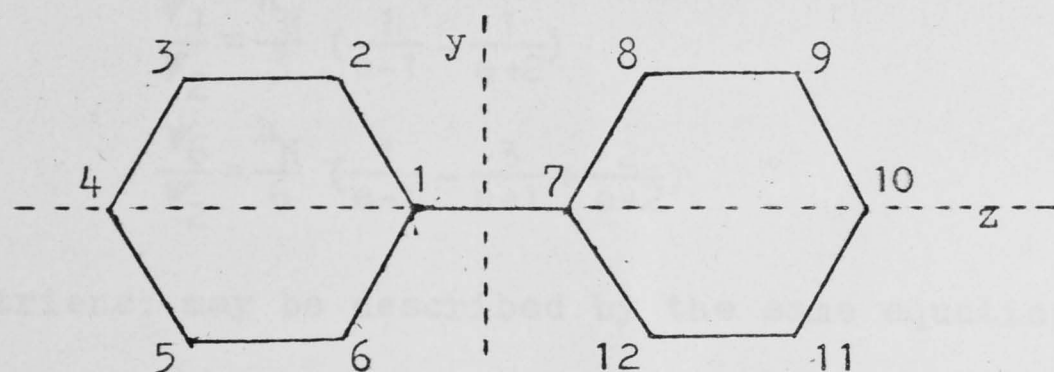
FIGURE 2-3: Numbering Schemes and Symmetry Planes of Group (a) Systems



Pyridine



Biphenylene



Biphenyl

Pyridazine: y-symmetric states

$$\frac{6}{h_N} = \frac{2}{e-2} + \frac{3}{e-1} + \frac{1}{e+1}$$

$$\frac{\psi_1}{\psi_2} = \frac{h_N}{3} \left(\frac{1}{e-2} - \frac{1}{e+1} \right)$$

$$\frac{\psi_6}{\psi_2} = \frac{h_N}{6} \left(\frac{2}{e-2} - \frac{3}{e-1} + \frac{1}{e+1} \right)$$

y-antisymmetric states

$$\frac{6}{h_N} = \frac{1}{e-1} + \frac{3}{e+1} + \frac{2}{e+2}$$

$$\frac{\psi_4}{\psi_2} = \frac{h_N}{3} \left(\frac{1}{e-1} - \frac{1}{e+2} \right)$$

$$\frac{\psi_6}{\psi_2} = \frac{h_N}{6} \left(\frac{1}{e-1} - \frac{3}{e+1} + \frac{2}{e+2} \right)$$

Hexatriene: may be described by the same equations as for pyridazine, with $h_N = +1$ for y-symmetric states, and $h_N = -1$ for y-antisymmetric states.

Biphenyl;

$$\pm \frac{6}{k_{17}} = \frac{1}{e-2} + \frac{2}{e-1} + \frac{2}{e+1} + \frac{1}{e+2}$$

y-symmetric states take the positive sign.

$$\frac{\psi_2}{\psi_1} = \frac{k_{17}}{6} \left(\frac{1}{e-2} + \frac{1}{e-1} - \frac{1}{e+1} - \frac{1}{e+2} \right)$$

$$\frac{\psi_3}{\psi_1} = \frac{k_{17}}{6} \left(\frac{1}{e-2} - \frac{1}{e-1} - \frac{1}{e+1} + \frac{1}{e+2} \right)$$

$$\frac{\psi_4}{\psi_1} = \frac{k_{17}}{6} \left(\frac{1}{e-2} - \frac{2}{e+1} + \frac{2}{e+1} - \frac{1}{e+2} \right)$$

There are also four states equivalent to benzene z-antisymmetric states.

Pyrazine: y-symmetric, z-symmetric.

$$\frac{3}{h_N} = \frac{1}{e-2} + \frac{2}{e+1} ; \frac{\psi_2}{\psi_1} = \frac{h_N}{3} \left(\frac{1}{e-2} - \frac{1}{e+1} \right)$$

y-antisymmetric, z-symmetric.

$$\frac{3}{h_N} = \frac{1}{e+2} + \frac{2}{e-1} ; \frac{\psi_2}{\psi_1} = \frac{h_N}{3} \left(\frac{1}{e-1} - \frac{1}{e+2} \right)$$

Biphenylene: y-symmetric, z-symmetric.

$$6 = \frac{2}{e-2} + \frac{3}{e-1} + \frac{1}{e+1} ;$$

$$\frac{\psi_1}{\psi_2} = \frac{1}{3} \left(\frac{1}{e-2} - \frac{1}{e+1} \right) ; \frac{\psi_6}{\psi_2} = \frac{1}{6} \left(\frac{2}{e-2} - \frac{3}{e-1} + \frac{1}{e+1} \right)$$

y-antisymmetric, z-symmetric.

$$6 = \frac{1}{e-1} + \frac{3}{e+1} + \frac{2}{e+2} ;$$

$$\frac{\psi_1}{\psi_2} = \frac{1}{3} \left(\frac{1}{e-1} - \frac{1}{e+2} \right) ; \frac{\psi_6}{\psi_2} = \frac{1}{6} \left(\frac{1}{e-1} - \frac{3}{e+1} + \frac{2}{e+2} \right)$$

y-symmetric, z-antisymmetric.

$$-6 = \frac{2}{e-2} + \frac{3}{e-1} + \frac{1}{e+1} ;$$

$$\frac{\psi_1}{\psi_2} = \frac{1}{3} \left(\frac{1}{e-2} - \frac{1}{e+1} \right) ; \frac{\psi_6}{\psi_2} = \frac{1}{6} \left(\frac{2}{e-2} - \frac{3}{e-1} + \frac{1}{e+1} \right)$$

y-antisymmetric, z-antisymmetric.

$$-6 = \frac{1}{e-1} + \frac{3}{e+1} + \frac{2}{e+2} ;$$

$$\frac{\psi_1}{\psi_2} = \frac{1}{3} \left(\frac{1}{e-1} - \frac{1}{e+2} \right) ; \frac{\psi_6}{\psi_2} = \frac{1}{6} \left(\frac{1}{e-1} - \frac{3}{e+1} + \frac{2}{e+2} \right)$$

Group (b): Systems derived from equations (18) and (16)

Aniline: (These equations also apply for phenol or benzyl.)

$$\frac{e-h_N}{k_{CN}} = \frac{\psi_1}{\psi_7} = \frac{k_{CN}}{6} \left(\frac{1}{e-2} + \frac{2}{e-1} + \frac{2}{e+1} + \frac{1}{e+2} \right)$$

$$\frac{\psi_2}{\psi_7} = \frac{k_{CN}}{6} \left(\frac{1}{e-2} + \frac{1}{e-1} - \frac{1}{e+1} - \frac{1}{e+2} \right)$$

$$\frac{\psi_3}{\psi_7} = \frac{k_{CN}}{6} \left(\frac{1}{e-2} - \frac{1}{e-1} - \frac{1}{e+1} + \frac{1}{e+2} \right)$$

$$\frac{\psi_4}{\psi_7} = \frac{k_{CN}}{6} \left(\frac{1}{e-2} - \frac{2}{e-1} + \frac{2}{e+1} - \frac{1}{e+2} \right)$$

There are also two states identical with benzene z-antisymmetric states.

Diphenylamine; y-symmetric, z-symmetric states.

$$\frac{e-h_N}{2k_{CN}} = \frac{\psi_1}{\psi_7} = \frac{k_{CN}}{6} \left(\frac{1}{e-2} + \frac{2}{e-1} + \frac{2}{e+1} + \frac{1}{e+2} \right)$$

Other equations as for aniline above.

The y-antisymmetric states are identical with the benzene states. The nitrogen centre does not contribute. There are also two y-symmetric, z-antisymmetric states which correspond to benzene z-antisymmetric states.

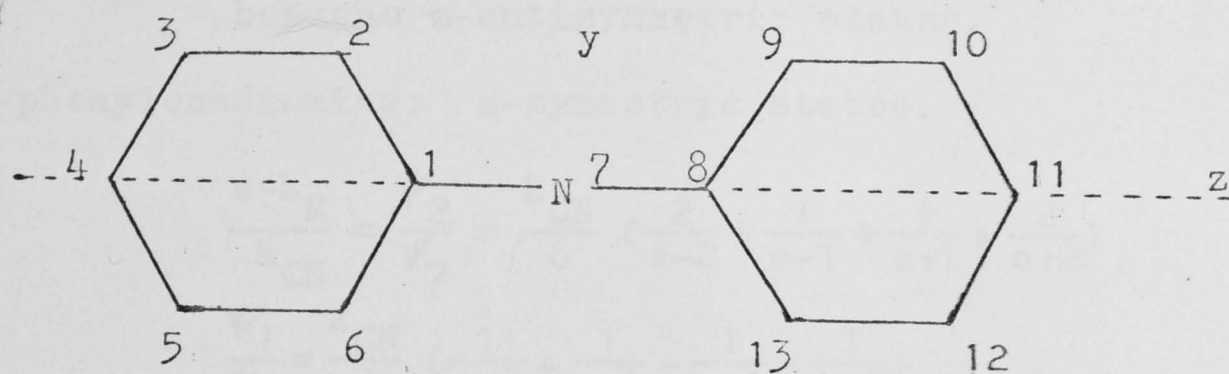
p-phenylenediamine: y-symmetric, z-symmetric states.

$$\frac{e-h_N}{k_{CN}} = \frac{\psi_1}{\psi_7} = \frac{k_{CN}}{3} \left(\frac{1}{e-2} + \frac{2}{e+1} \right) ; \frac{\psi_2}{\psi_7} = \frac{k_{CN}}{3} \left(\frac{1}{e-2} - \frac{1}{e+1} \right)$$

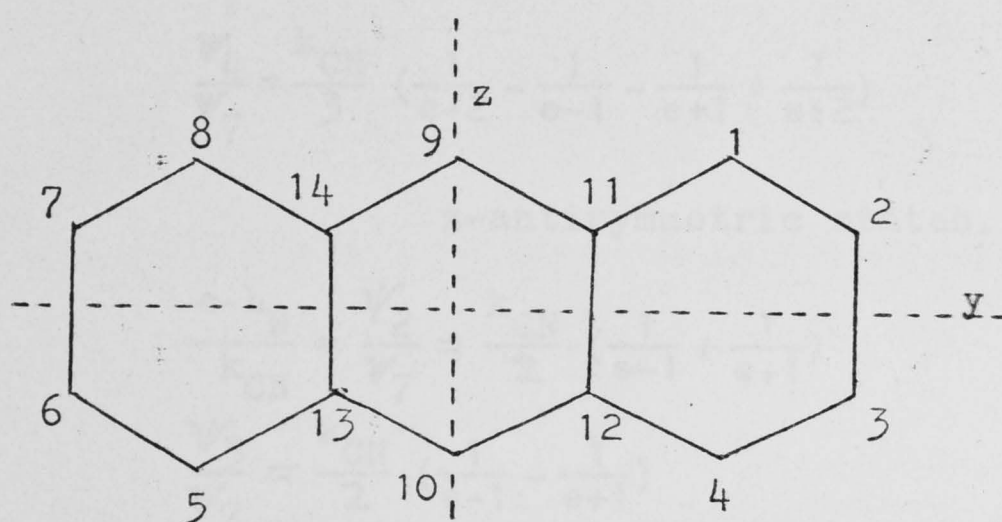
y-antisymmetric, z-symmetric states.

$$\frac{e-h_N}{k_{CN}} = \frac{\psi_1}{\psi_7} = \frac{k_{CN}}{3} \left(\frac{2}{e-1} + \frac{1}{e+2} \right) ; \frac{\psi_2}{\psi_7} = \frac{k_{CN}}{3} \left(\frac{1}{e-1} - \frac{1}{e+2} \right)$$

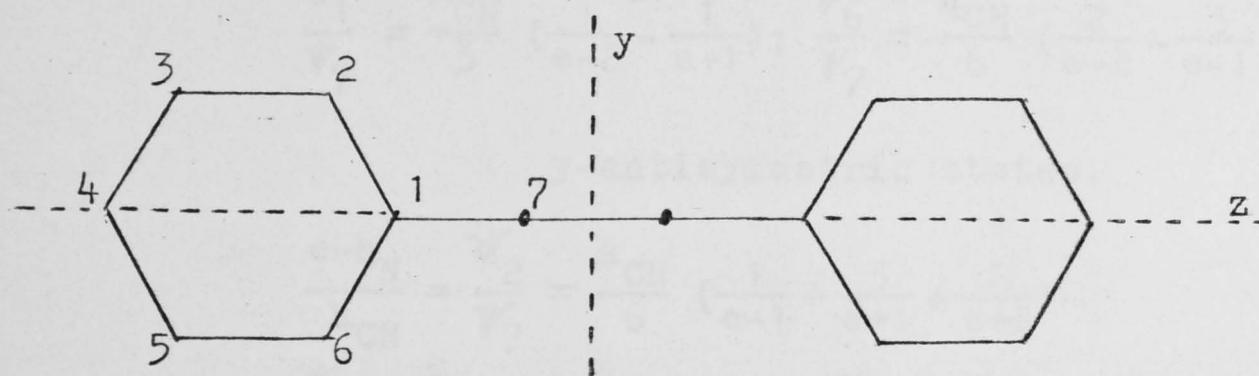
FIGURE 2-4: Numbering and Planes for Group (b) Systems



Diphenylamine



Anthracene



Stilbene

p-phenylenediamine: There are also two states identical with benzene z-antisymmetric states.

m-phenylenediamine: z-symmetric states.

$$\frac{e-h_N}{k_{CN}} = \frac{\psi_2}{\psi_7} = \frac{k_{CN}}{6} \left(\frac{2}{e-2} + \frac{1}{e-1} + \frac{1}{e+1} + \frac{2}{e+2} \right)$$

$$\frac{\psi_1}{\psi_7} = \frac{k_{CN}}{3} \left(\frac{1}{e-2} + \frac{1}{e-1} - \frac{1}{e+1} - \frac{1}{e+2} \right)$$

$$\frac{\psi_3}{\psi_7} = \frac{k_{CN}}{6} \left(\frac{2}{e-2} - \frac{1}{e-1} + \frac{1}{e+1} - \frac{2}{e+2} \right)$$

$$\frac{\psi_4}{\psi_7} = \frac{k_{CN}}{3} \left(\frac{1}{e-2} - \frac{1}{e-1} - \frac{1}{e+1} + \frac{1}{e+2} \right)$$

z-antisymmetric states.

$$\frac{e-h_N}{k_{CN}} = \frac{\psi_2}{\psi_7} = \frac{k_{CN}}{2} \left(\frac{1}{e-1} + \frac{1}{e+1} \right)$$

$$\frac{\psi_3}{\psi_7} = \frac{k_{CN}}{2} \left(\frac{1}{e-1} - \frac{1}{e+1} \right)$$

o-phenylenediamine: y-symmetric states.

$$\frac{e-h_N}{k_{CN}} = \frac{\psi_2}{\psi_7} = \frac{k_{CN}}{6} \left(\frac{2}{e-2} + \frac{3}{e-1} + \frac{1}{e+1} \right)$$

$$\frac{\psi_1}{\psi_7} = \frac{k_{CN}}{3} \left(\frac{1}{e-2} - \frac{1}{e+1} \right); \quad \frac{\psi_6}{\psi_7} = \frac{k_{CN}}{6} \left(\frac{2}{e-2} - \frac{3}{e-1} + \frac{1}{e+1} \right)$$

y-antisymmetric states.

$$\frac{e-h_N}{k_{CN}} = \frac{\psi_2}{\psi_7} = \frac{k_{CN}}{6} \left(\frac{1}{e-1} + \frac{3}{e+1} + \frac{2}{e+2} \right)$$

$$\frac{\psi_1}{\psi_7} = \frac{k_{CN}}{3} \left(\frac{1}{e-1} - \frac{1}{e+2} \right); \quad \frac{\psi_6}{\psi_7} = \frac{k_{CN}}{6} \left(\frac{1}{e-1} - \frac{3}{e+1} + \frac{2}{e+2} \right)$$

Stilbene: For y-symmetric states the equations for aniline apply with $k_{CN} \approx 1$ and $h_N \approx 1$. For y-antisymmetric

states the same equations apply with $h_N = -1$.

Anthracene: z-symmetric, y-symmetric states.

$$\frac{e}{2} = \frac{\psi_{11}}{\psi_9} = \frac{1}{6} \left(\frac{2}{e-2} + \frac{3}{e-1} + \frac{1}{e+1} \right)$$

$$\frac{\psi_1}{\psi_9} = \frac{1}{3} \left(\frac{1}{e-2} - \frac{1}{e+1} \right) ; \frac{\psi_2}{\psi_9} = \frac{1}{6} \left(\frac{2}{e-2} - \frac{3}{e-1} + \frac{1}{e+1} \right)$$

z-symmetric, y-antisymmetric states.

$$\frac{e}{2} = \frac{\psi_{11}}{\psi_9} = \frac{1}{6} \left(\frac{1}{e-1} + \frac{3}{e+1} + \frac{2}{e+2} \right)$$

$$\frac{\psi_1}{\psi_9} = \frac{1}{3} \left(\frac{1}{e-1} - \frac{1}{e+2} \right) ; \frac{\psi_2}{\psi_9} = \frac{1}{6} \left(\frac{1}{e-1} - \frac{3}{e+1} + \frac{2}{e+2} \right)$$

The six z-antisymmetric states correspond to the six benzene states.

Group (c): Systems derived from equations (19) and (16).

Styrene:

$$e - \frac{1}{e} = \frac{\psi_1}{\psi_7} = \frac{1}{6} \left(\frac{1}{e-2} + \frac{2}{e-1} + \frac{2}{e+1} + \frac{1}{e+2} \right) ; \frac{\psi_1}{\psi_8} = e^2 - 1$$

$$\frac{\psi_2}{\psi_7} = \frac{1}{6} \left(\frac{1}{e-2} + \frac{1}{e-1} - \frac{1}{e+1} - \frac{1}{e+2} \right)$$

$$\frac{\psi_3}{\psi_7} = \frac{1}{6} \left(\frac{1}{e-2} - \frac{1}{e-1} - \frac{1}{e+1} + \frac{1}{e+2} \right)$$

$$\frac{\psi_4}{\psi_7} = \frac{1}{6} \left(\frac{1}{e-2} - \frac{2}{e-1} + \frac{2}{e+1} - \frac{1}{e+2} \right)$$

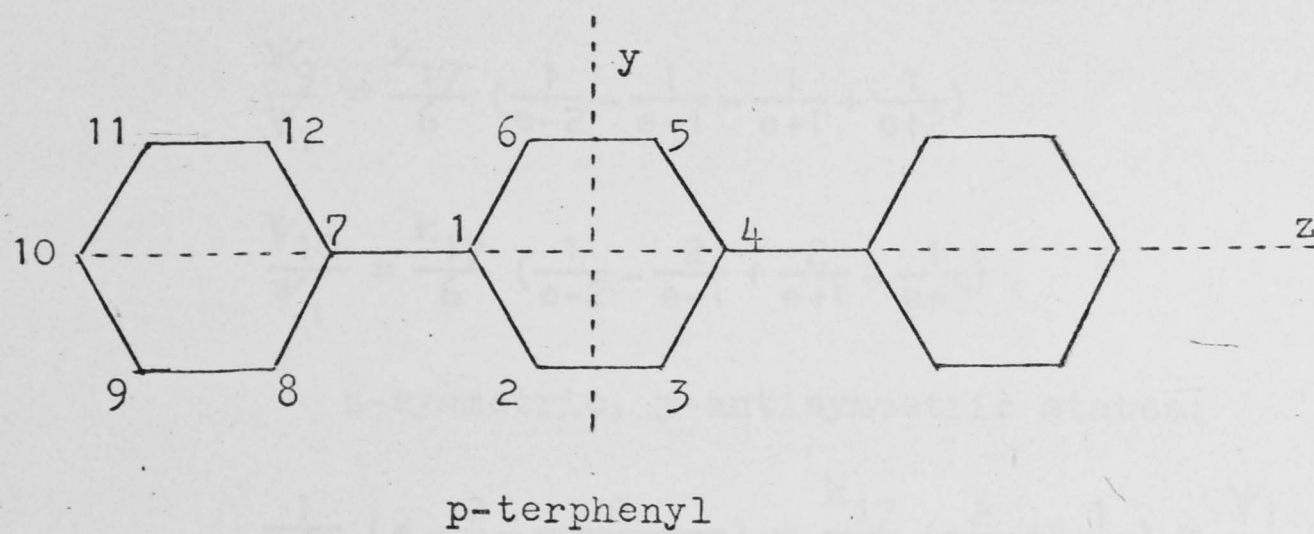
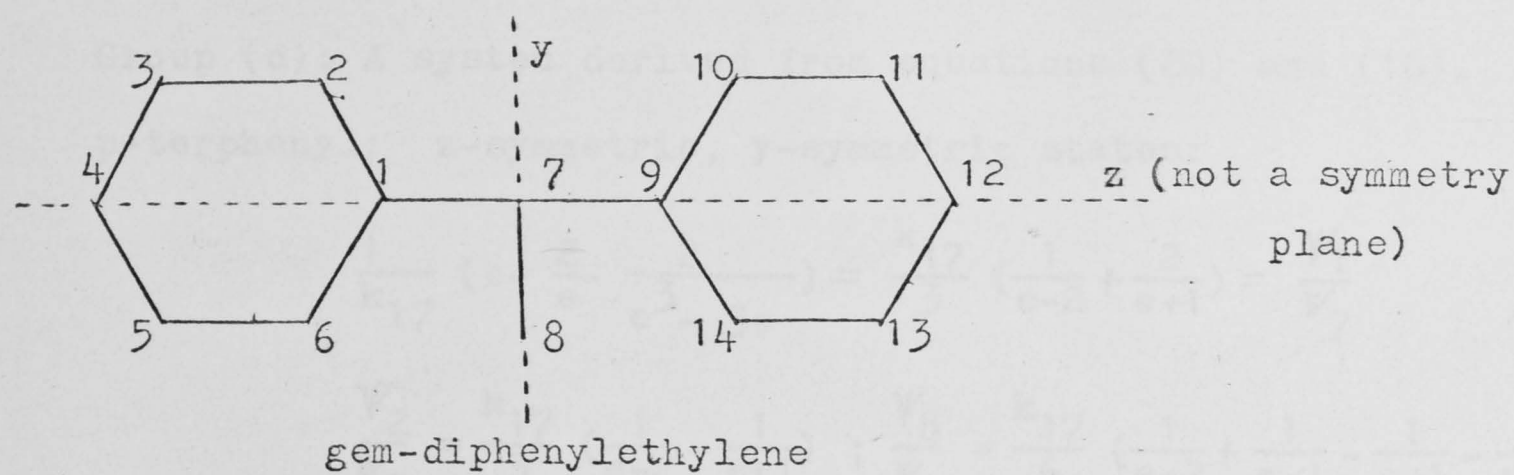
There are also two states identical with benzene z-antisymmetric states.

gem-diphenylethylene: y-symmetric, z-symmetric states.

$$e - \frac{1}{e} = \frac{1}{3} \left(\frac{1}{e-2} + \frac{2}{e-1} + \frac{2}{e+1} + \frac{1}{e+2} \right) = 2 \frac{\psi_1}{\psi_7}$$

with other equations as for styrene.

FIGURE 2-5: Numbering and Planes of Other Systems



gem-diphenylethylene: y-antisymmetric states are equivalent to benzene states. The two y-symmetric, z-antisymmetric states are equivalent to benzene z-antisymmetric states.

Group (d): A system derived from equations (20) and (16).

p-terphenyl: z-symmetric, y-symmetric states:

$$\frac{1}{k_{17}} \left(e - \frac{2}{e} - \frac{2}{e^3 - 3e} \right) = \frac{k_{17}}{3} \left(\frac{1}{e-2} + \frac{2}{e+1} \right) = \frac{\psi_1}{\psi_7}$$

$$\frac{\psi_2}{\psi_7} = \frac{k_{17}}{3} \left(\frac{1}{e-2} - \frac{1}{e+1} \right) ; \frac{\psi_8}{\psi_1} = \frac{k_{17}}{6} \left(\frac{1}{e-2} + \frac{1}{e-1} - \frac{1}{e+1} - \frac{1}{e+2} \right)$$

$$\frac{\psi_9}{\psi_1} = \frac{k_{17}}{6} \left(\frac{1}{e-2} - \frac{1}{e-1} - \frac{1}{e+1} + \frac{1}{e+2} \right)$$

$$\frac{\psi_{10}}{\psi_1} = \frac{k_{17}}{6} \left(\frac{1}{e-2} - \frac{2}{e-1} + \frac{2}{e+1} - \frac{1}{e+2} \right)$$

z-symmetric, y-antisymmetric states:

$$\frac{1}{k_{17}} \left(e - \frac{2}{e} - \frac{2}{e^3 - 3e} \right) = \frac{k_{17}}{3} \left(\frac{2}{e-1} + \frac{1}{e+2} \right) = \frac{\psi_1}{\psi_7}$$

$$\frac{\psi_2}{\psi_7} = \frac{k_{17}}{3} \left(\frac{1}{e-1} - \frac{1}{e+2} \right), \text{ with other equations as above.}$$

The six z-antisymmetric states correspond to three degenerate pairs of benzene z-antisymmetric states.

CHAPTER 3: SUBSTITUENT EFFECTS IN THE CYCLIC PHOSPHONITRILIC COMPOUNDS

(i) The Electronic Structure of the Cyclic Phosphonitriles

When phosphorus pentachloride is reacted with ammonium chloride in an organic solvent, a large variety of products is formed, including a series of compounds with the molecular formula $(\text{NPCl}_2)_n$ ³⁵⁻³⁷. Stokes isolated these compounds for $n = 3$ to $n = 7$ ³⁶. The octamer was later isolated³⁸ and evidence was produced that the series continued to much higher n . It has been shown that the compounds have cyclic structures, with nitrogen and phosphorus atoms alternating around an even-membered ring. Two chlorine atoms are bonded exocyclically to each phosphorus atom so as to complete an approximately tetrahedral coordination at phosphorus. Many similar compounds have been prepared, in which some or all of the chlorine atoms are replaced by other monovalent groups (typically bromine, fluorine, alkyl, alkoxy, aryl, and amine substituents). In some cases, notably the fluorides, larger ring compounds have been prepared and isolated. The chemistry of these compounds has been studied extensively in recent years, and much is known of their physical and chemical properties^{37,39}. The halides undergo reactions typical of acid halides, but their reaction rates are slower. Many derivatives may be prepared by direct nucleophilic substitution of the chlorides. The ring

structure tends to be preserved in most reactions - even in those requiring quite harsh conditions.

The electronic structure of the compounds is interesting in that it involves pi bonding between 3d orbitals centred on phosphorus and 2p orbitals centred on nitrogen⁴⁰⁻⁴³. Furthermore, as all bond lengths are equal to within the experimental error, in the structures which have been determined, and as these lengths are intermediate between the bond lengths expected for a single P-N bond and those expected for a double P=N bond, some type of delocalized pi bonding must be invoked. The pi bonds are fairly weak in comparison with the more familiar pi bonds encountered in conjugated carbon compounds. An estimate has been made⁴² that the energy of the P-N bonds in $(\text{NPCl}_2)_3$ is some 6-10 Kcal./mole higher than would be expected for single P-N bonds in a similar structure. For benzene, the corresponding figure is about 38 Kcal./mole.

The electronic structure of the cyclic phosphonitriles may be considered in a simple valence bond picture. Each phosphorus atom donates four of its valence electrons in 3sp^3 orbitals in forming single bonds with the tetrahedrally disposed ligands: two ring nitrogen atoms, and two atoms from the exocyclic substituents. The fifth electron must then be accommodated in a higher energy orbital. Each nitrogen atom may be regarded as donating two 2sp^2 valence electrons to sigma bonding with the neighbouring phosphorus atoms. Two of

the remaining electrons are then assigned as a lone pair to the third $2sp^2$ orbital, and the fifth valence electron is assigned to the $2p_z$ orbital. The lowest available orbitals for the fifth phosphorus valence electron are the $3d$ and $4s$ orbitals. Of these, only the $3d_{xz}$ and $3d_{yz}$ orbitals can form π bonds with the nitrogen $2p_z$ orbitals, as the overlap of the other $3d$ and $4s$ orbitals with $2p_z$ is zero by symmetry. (This is true only for planar systems. Non-planarity of the phosphonitrile ring introduces perturbations.) Throughout the discussion in this chapter the axis system used by Craig, Paddock, and Mitchell⁴⁴ is adopted. The xy plane for any ring atomic centre is the plane containing the two ring sigma bonds. The y axis is the axis which bisects the angle formed by these bonds.

Craig and Paddock^{40,41} investigated the π system which would arise from a cyclic delocalization involving $2p_z$ orbitals on nitrogen, and $3d_{xz}$ orbitals on phosphorus, using symmetry arguments expressed in a simple Hückel framework. Dewar, Lucken, and Whitehead⁴⁵ on the other hand, implicitly assumed that the $3d_{xz}$ and the $3d_{yz}$ orbitals on phosphorus were equally available for π bonding. From these orbitals they derived a pair of hybrid d -orbitals centred on each phosphorus atom, such that each overlapped strongly with one of the neighbouring nitrogen $2p_z$ orbitals, and negligibly with the other. In this way the ring systems of various sizes are all described by a series of "island" π systems, each

delocalized over three centres, incorporating two phosphorus 3d orbitals and one nitrogen $2p_z$ orbital in its basis set. Craig and Mitchell⁴⁴ emphasized that this island model was only a special case of the more general scheme which could be obtained by allowing both $3d_{xz}$ and $3d_{yz}$ orbitals on phosphorus to participate in a cyclically delocalized pi system, and showed that it is only a realistic picture for a particular narrow range of relative participation by the two types of phosphorus d orbital. Later calculations by Mitchell, in which he considered ligand effects and the effects of exchange forces in deriving optimum sizes for the phosphorus d orbitals⁴⁶, showed that only the $3d_{xz}$ orbital was sufficiently compact to have a large overlap with a nitrogen $2p_z$ orbital. This provides a strong indication that the $3d_{xz}$ is the major contributing phosphorus orbital to the out-of-plane pi structure.

Meanwhile, it had been proposed that another type of pi bonding could contribute markedly to the structure of the phosphonitriles⁴⁷⁻⁴⁹. The lone pair trigonal orbitals on the nitrogen atoms are in a position to overlap with some of the 3d orbitals centred on the neighbouring phosphorus atoms. Delocalization of the nitrogen lone pair electrons into molecular orbitals involving these 3d orbitals could occur. This delocalization would increase the stability of the system. The large ring angles often found at nitrogen centres in the phosphonitrilic compounds can be accounted for by this

type of interaction⁵⁰. Mitchell's calculations⁴⁶ show that, of the d orbitals, only the $3d_{x^2-y^2}$ is likely to play a significant part in this type of interaction. $3d_{xy}$ and $3d_z^2$ orbitals are unlikely to be important, both because of unfavourable orientation, and because the optimum size of these orbitals in the ligand field is very large.

Thus the indications are that a suitable simple model for the pi bonding in the phosphonitrilic compounds (for planar systems, at least) would consider two orthogonal cyclically delocalized pi systems. One would provide electron density in the plane of the phosphonitrile ring, and is formed from a basis set of nitrogen $2sp^2$ and contracted phosphorus $3d_{x^2-y^2}$ atomic orbitals. The other would provide electron density above and below the ring plane, and would use a basis set of nitrogen $2p_z$ and contracted phosphorus $3d_{xz}$ atomic orbitals.

The known crystal structures of the trimeric compounds all indicate planar phosphonitrile rings in these compounds. The tetrameric octafluorophosphonitrile is also planar. The few pentamer structures which are known have phosphonitrile rings close to planar, with two "inward pointing" nitrogen atoms. The non-planarity is slight, and seems to be governed by the steric requirements of the "inward" nitrogen atoms. Most tetramer structures are intermediate between the "tub" form and one of the "saddle" forms. These forms are related by what is probably a free internal deformation in fluid

phases. The saddle form, which most systems approximate, has small dihedral angles, which are further reduced by the tendency for the PNP angle to be much larger than the normal 120° . It appears, then, that the molecules are as close to planar as steric factors will allow⁵¹, and that a planar model in a simple molecular orbital picture is probably an acceptable approximation⁴¹.

The phosphonitrilic compounds are interesting, then, from the point of view of electronic structure, for several reasons. They form a large and varied group of inorganic compounds having delocalized pi systems. They provide an example of pi bonding between $2p_z$ and $3d_{xz}$ orbitals. These orbitals have different symmetry properties, which lead to a different type of interaction in a cyclic pi system. The effect is to change the sign of alternate resonance integrals around the ring. This results in several differences in energy levels and electronic structure between heteromorphic systems of this type and the homomorphic systems familiar in $p\pi-p\pi$ bonding. The systems also have, however, a second pi system arising from $d\pi-p\pi$ interactions of a homomorphic type. Various properties of the substances may reflect the influence of either or both of these systems. Finally, the molecules are interesting because of the large effects of ligands on d orbitals^{50,52}. The effects of substituents on the pi systems of the phosphonitrilic compounds may be quite large, despite the comparative weakness of the pi bonding.

In this chapter, substituent effects in the phosphonitrilic compounds are examined in terms of a very simple molecular orbital model, using the techniques explored in chapter 2. Broad qualitative comparisons are made between the electron distributions suggested by the model, and some of the known physical and chemical properties of the phosphonitrilic compounds.

(ii) A Hückel Molecular Orbital Description of the Symmetrical Phosphonitriles

A simple description of the π electronic structure of the phosphonitrilic compounds can be obtained from the Hückel molecular orbital treatment, if it is assumed that the phosphonitrile rings are planar. Deviations from planarity introduce mixing of the two π systems, as well as slightly changing the resonance integrals. Moreover, the situation may be further complicated by the introduction of an important role for the $3d_{yz}$ and $3d_{xy}$ orbitals on phosphorus. In non-planar structures these orbitals may be contracted more by the ligand field, and they may also be more suitably oriented to overlap with the orbitals centred on the neighbouring nitrogen atoms. The introduction of several more unknown or empirically assigned parameters would be necessary to account for these features of a non-planar model in a Hückel treatment. This constitutes a disadvantage which seems to outweigh any probable advantage of the more realistic

geometry of the non-planar model. The planar model is unlikely to be greatly in error, as deviations from planarity are small, and appear to be related primarily to steric influences. Craig⁴¹ has suggested that $d\pi$ - $p\pi$ bonding should be less sensitive to non-planarity than is $p\pi$ - $p\pi$ bonding.

For the π system in a symmetrically substituted phosphonitrilic compound, the matrix elements for a Hückel treatment are conveniently parametrized as follows.

Out-of-plane π system

$$\langle \chi_N(2p_z) | H | \chi_P(3d_{xz}) \rangle = \beta \quad \text{for bonded P and N.}$$

$$\langle \chi_N(2p_z) | H | \chi_N(2p_z) \rangle = \alpha + \sigma\beta$$

$$\langle \chi_P(3d_{xz}) | H | \chi_P(3d_{xz}) \rangle = \alpha - \sigma\beta$$

In-plane π system

$$\langle \chi_N(2sp^2) | H | \chi_P(3d_{x^2-y^2}) \rangle = \beta' \quad \text{for bonded P and N.}$$

$$\langle \chi_N(2sp^2) | H | \chi_N(2sp^2) \rangle = \alpha' + \sigma'\beta'$$

$$\langle \chi_P(3d_{x^2-y^2}) | H | \chi_P(3d_{x^2-y^2}) \rangle = \alpha' - \sigma'\beta'$$

The orbitals centred on nitrogen are more electronegative than those centred on phosphorus, and so σ and σ' will, in general, be positive. For the in-plane π system the eigenvalues and eigenfunctions are given by⁴¹

$$E'_k = \alpha' \pm \beta' \sqrt{\sigma'^2 + 4 \cos^2 2\pi k/n} \quad (\text{the sign of } \cos 2\pi k/n \text{ is taken})$$

$$c'_{1k} = \sqrt{(e'_k + \sigma')/ne'_k} \cdot e^{2\pi i(1-1)k/n} \quad \text{for nitrogen orbitals.}$$

$$c'_{1k} = \sqrt{(e'_k - \sigma')/ne'_k} \cdot e^{2\pi i(1-1)k/n} \quad \text{for phosphorus orbitals.}$$

For the heteromorphic system formed from the out-of-plane

pi orbitals the expressions differ in form. Similar simple expressions can, however, be obtained⁴¹.

$$E_k = \alpha \pm \beta \sqrt{\sigma^2 + 4 \sin^2 2\pi k/n} \quad (\text{the sign of } \sin 2\pi k/n \text{ is taken})$$

$$c_{lk} = \sqrt{(e_k + \sigma)/ne_k} \cdot e^{2\pi i(1-l)(k/n - 1/4)} \quad \text{for nitrogen orbitals.}$$

$$c_{lk} = \sqrt{(e_k - \sigma)/ne_k} \cdot e^{2\pi i(1-l)(k/n - 1/4)} \quad \text{for phosphorus orbitals.}$$

In the previous expressions, n is the number of atoms in the phosphonitrile ring, k and l range from 1 to n , and e'_k and e_k are measures of the energy of the k -th. molecular orbital in the out-of-plane and the in-plane pi systems, respectively.

$$e_k = (E_k - \alpha)/\beta \quad ; \quad e'_k = (E'_k - \alpha')/\beta'$$

In applying the treatment of chapter 2, it is convenient to choose eigenfunctions with real coefficients, and a symmetry plane passing through the atomic centres numbered 1 and $n/2 + 1$. This is achieved by replacing the eigenfunctions of the degenerate pairs of levels in the following way: each degenerate eigenvalue has a pair of orthogonal eigenfunctions whose coefficients are given in the above scheme by

$$c_{lk} = a e^{ib} \quad \text{and} \quad c_{(n-l)k} = a e^{-ib}$$

The required pair of eigenfunctions, having real coefficients and the appropriate symmetry plane, are obtained by replacing these coefficients with

$$c_{lk}^{\text{symm}} = \sqrt{2} a \cos b \quad \text{and} \quad c_{lk}^{\text{anti}} = \sqrt{2} a \sin b$$

Levels which are not degenerate have coefficients which are already real, or which are pure imaginary, and can be made real by a simple scalar multiplication. All of the systems can thus be expressed in terms of this choice of eigenfunctions, and the equations derived in chapter 2 may be applied directly to obtain a series of model results for phosphonitrilic compounds containing one phosphorus site substituted differently to the others.

(iii) Model Calculations for Phosponitriles Disturbed at a Single Site

There is good evidence that 3d orbitals in second row elements such as silicon, phosphorus, and sulphur, are very sensitive in size and electronegativity to the nature of the ligands which are bound to the atomic centre in a molecule. Substituent effects in the phosphonitrilic compounds may be regarded in this light. A phosphonitrile which is not symmetrically substituted may have d-orbitals of different sizes and energies on the different phosphorus sites. Hückel calculations would require different coulomb and resonance integrals for these phosphorus sites. The orientation of the exocyclic ligands is such that overlap can also occur between ligand pi orbitals and phosphorus 3d orbitals, leading to some mixing of the ligand pi system with the phosphonitrile pi system. Mitchell's calculations show that the only interaction of this type which is important is an overlap of

the ligand pi orbitals with phosphorus $3d_{x^2-y^2}$. The in-plane pi system may, therefore, be affected significantly by an extended pi interaction with a suitable ligand. It is a familiar result of simple molecular orbital theory, though, that such effects can usually be adequately treated by simply changing the coulomb integral of the site where the interaction occurs, so that this site becomes effectively a source or a sink of electron density. This is particularly the case when the ligand pi system is localized on a single site, as it would be for amine or alkoxy substituted phosphonitriles. The calculations presented in this section therefore treat ligand effects as a change in the coulomb integrals of the basis orbitals centred on the disturbed phosphorus site. This change may arise from two sources: different orbital contraction produced by the different ligands on the disturbed site, and possibly also by differences in the presence or the structure of ligand pi systems which interact with the ring pi system.

The variations in size of the phosphorus orbitals would also affect overlap, and hence resonance integrals. Mitchell's calculations show, however, that the orbital contraction is such that the $3d_{x^2-y^2}$ and $3d_{xz}$ functions have optimum exponents similar to those which would produce an overlap maximum with neighbouring nitrogen pi orbitals. The variations in these exponents due to the effects of different ligands are unlikely to produce large changes in

overlap. It is assumed, then, that changes in resonance integrals are secondary effects which are fairly small. Inclusion of these effects in the model would require the introduction of more arbitrary parameters, without greatly improving the treatment.

The general phosphonitrilic compound substituted at one phosphorus site, may be regarded in this Huckel model as being equivalent to the corresponding symmetrical compound, carrying a disturbance of $\rho\beta$ on the $3d_{xz}$ orbital coulomb integral at the substituted phosphorus site, and a disturbance of $\rho'\beta'$ on the $3d_{x^2-y^2}$ orbital coulomb integral. Equations (10) and (11) of chapter 2 may then be applied directly, using as eigenfunctions of the undisturbed system those of symmetrically substituted phosphonitriles presented in the previous section.

A series of calculations was performed in this way for the parameter values: $\sigma' = 0.0$ by 0.2 to 1.4 ; $\rho' = -1.0$ by 0.1 to 1.0 ; for trimer, tetramer, pentamer, and hexamer; $\sigma = 0.0$ by 0.2 to 1.4 ; $\rho = -1.0$ by 0.1 to 1.0 ; for trimer and pentamer. The heteromorphic tetramer and hexamer differ from the homomorphic only in the sign of some of the coefficients. The computer time required was about 15% of that which would have been required to obtain the same results by a series of matrix diagonalizations. Some of the results of the calculations are presented in the succeeding figures and tables.

In table 3-1 the electron densities in the symmetrical phosphonitriles are tabulated for various values of the difference in coulomb integral between the nitrogen and phosphorus orbitals. The electron distribution varies considerably for the different ring sizes and for the different types of pi bonding. The variation of these electron densities is typical of the variation of most molecular orbital quantities. In the homomorphic systems an alternation of electron densities with ring size is apparent, analogous to the alternation described in Hückel's law⁸⁻¹¹. The order of decreasing electron density on phosphorus is trimer > pentamer > hexamer > tetramer. In the heteromorphic pi systems, on the other hand, Hückel's law does not apply⁴¹, and a gradation of the electron densities with ring size occurs. In these systems the order of decreasing electron density on phosphorus is hexamer > pentamer > tetramer > trimer. In both cases, increasing the parameter σ (half the electronegativity difference between phosphorus and nitrogen orbitals) leads to a much more rapid convergence of properties with increasing ring size. In the region $\sigma = 1.0$ to 1.4 the convergence becomes so rapid that "alternation" or "gradation" of properties with increasing ring size is no longer an appropriate description. It is more accurate to say that the properties of the larger systems are all very similar, while those of the trimer differ somewhat. This applies to both the homomorphic and the heteromorphic pi systems.

Table 3-1: Electron Density on Phosphorus in Symmetrical
Phosphonitriles

homomorphic system

σ'	trimer	tetramer	pentamer	hexamer
0.0	1.0	1.0(0.750)	1.0	1.0(0.833)
0.2	0.836	0.655	0.808	0.713
0.4	0.687	0.544	0.647	0.602
0.6	0.561	0.483	0.525	0.505
0.8	0.460	0.411	0.432	0.423
1.0	0.380	0.349	0.360	0.356
1.2	0.316	0.298	0.303	0.302
1.4	0.266	0.255	0.258	0.257

heteromorphic system

σ	trimer	tetramer	pentamer	hexamer
0.0	1.0(0.667)	1.0(0.750)	1.0(0.800)	1.0(0.833)
0.2	0.590	0.655	0.691	0.713
0.4	0.517	0.544	0.589	0.602
0.6	0.448	0.483	0.498	0.505
0.8	0.387	0.411	0.420	0.423
1.0	0.333	0.349	0.355	0.356
1.2	0.287	0.298	0.300	0.302
1.4	0.248	0.255	0.257	0.257

The effects of a disturbance at a phosphorus atom on the electron distribution in the pi systems are shown in figures 3-1 to 3-4. In the trimeric homomorphic system, the changes in electron density on the disturbed phosphorus orbital are compensated in the N_2 and N_4 electron densities; there is almost no change in the electron density on P_3 . In the limit $\sigma = 0$ this is the charge redistribution pattern of the substituted benzene derivatives. As the electronegativity difference parameter, σ , increases, the compensation is obtained to a greater extent from N_2 , and the changes in

electron density on N_4 become small. For all of the other systems, however, the electron density redistribution only affects the substituted phosphorus orbital, P_1 , and the adjacent nitrogen orbitals, N_2 , to any great extent. Effects on more remote centres are comparatively small, and are fairly similar for nitrogen or phosphorus orbitals. This behaviour is very similar to that predicted by the "island model" of Dewar⁴⁵. The delocalized pi system does not necessarily lead to long range effects in such quantities as the pi electron density, even though in many cases it may do so. Conversely, an absence of long range effects does not necessarily argue against a cyclically delocalized pi system. In the phosphonitriles there are effects which are difficult to explain using the island model. These include alternations in such properties as ionization potential with ring size, as well as the reactivities discussed in the next section.

Table 3-2 is presented as a matter of theoretical interest, rather than for any practical interest as a model of the phosphonitriles. It is apparent that the localized nature of the charge redistribution in the larger systems does not persist to zero electronegativity difference. Indeed, the large rings have a very complex long range charge redistribution pattern at low electronegativity difference. These long range redistributions fall off much more rapidly with increasing electronegativity difference in the larger systems than does the effect on N_4 in the trimeric system.

Table 3-2: Electron Density Changes with a Disturbance

 $\sigma = 1$ on Phosphorus

Site	Trimer		Tetramer	Pentamer		Hexamer
	homo.	hetero.		homo.	hetero.	
$\sigma = 0.0$						
P ₁	.3697	.3018	.3454	.4002	.3600	.3746
N ₂	-.1452	-.0616	-.0783	-.1302	-.0817	-.0880
P ₃	.0082	-.0893	-.0525	.0241	-.0297	-.0144
N ₄	-.0956	0	-.0046	-.0666	-.0105	-.0152
P ₅			-.0746	.0018	-.0571	-.0436
N ₆				-.0584	0	-.0014
P ₇						-.0494
$\sigma = 0.6$						
P ₁	.3406	.2589	.3019	.3409	.3208	.3263
N ₂	-.1398	-.0971	-.1195	-.1287	-.1232	-.1251
P ₃	.0035	-.0323	-.0189	.0020	-.0111	-.0073
N ₄	-.0681	0	-.0076	-.0327	-.0149	-.0190
P ₅			-.0199	-.0003	-.0112	-.0073
N ₆				-.0207	0	-.0015
P ₇						-.0057

The patterns of electron density redistribution for a disturbance at position 1 with $\sigma = 0$ are recorded here:

homomorphic trimer : position 2 > position 4

heteromorphic trimer : position 3 > position 2

tetramer : position 2 ~ position 5 > position 3

homomorphic pentamer : position 2 > position 4 ~ position 6

heteromorphic pentamer: position 2 > position 5 > position 3

hexamer : position 2 > position 7 ~ position 5.

In figures 3-5 and 3-6 the effects of a disturbance at one phosphorus site, on the electron densities at the other phosphorus-centred orbitals, are shown in more detail. The effects are fairly small, but they may play an important part in some of the properties of the substituted phosphonitrilic compounds. In the homomorphic systems there is a marked difference between the trimer and pentamer on the one hand, and the tetramer and hexamer on the other. Again, the differences between the systems diminish markedly with increasing electronegativity difference. Figures 3-7 to 3-10 show the changes in electron density on the various phosphorus centres as a function of the electronegativity difference, for a fixed size of disturbance on the phosphorus centre.

Finally, typical plots of variation of total π bonding energy, and of π bond orders are presented. These quantities appear rather more to be artifacts of the particular molecular orbital scheme chosen than are the electron densities. In particular, the assumption of zero overlap between neighbouring basis orbitals, rather than a more realistic value, could lead to unrealistic comparisons between the bonding energies of the various systems, while the bond orders (unlike the electron densities) are very sensitive to the small changes in resonance integrals, which have been neglected. The π -bonding energy plotted in the graphs is defined as the difference between the total π energy and

FIG. 3-1: Homomorphic System in $(NPX_2)_2(NPY_2)$

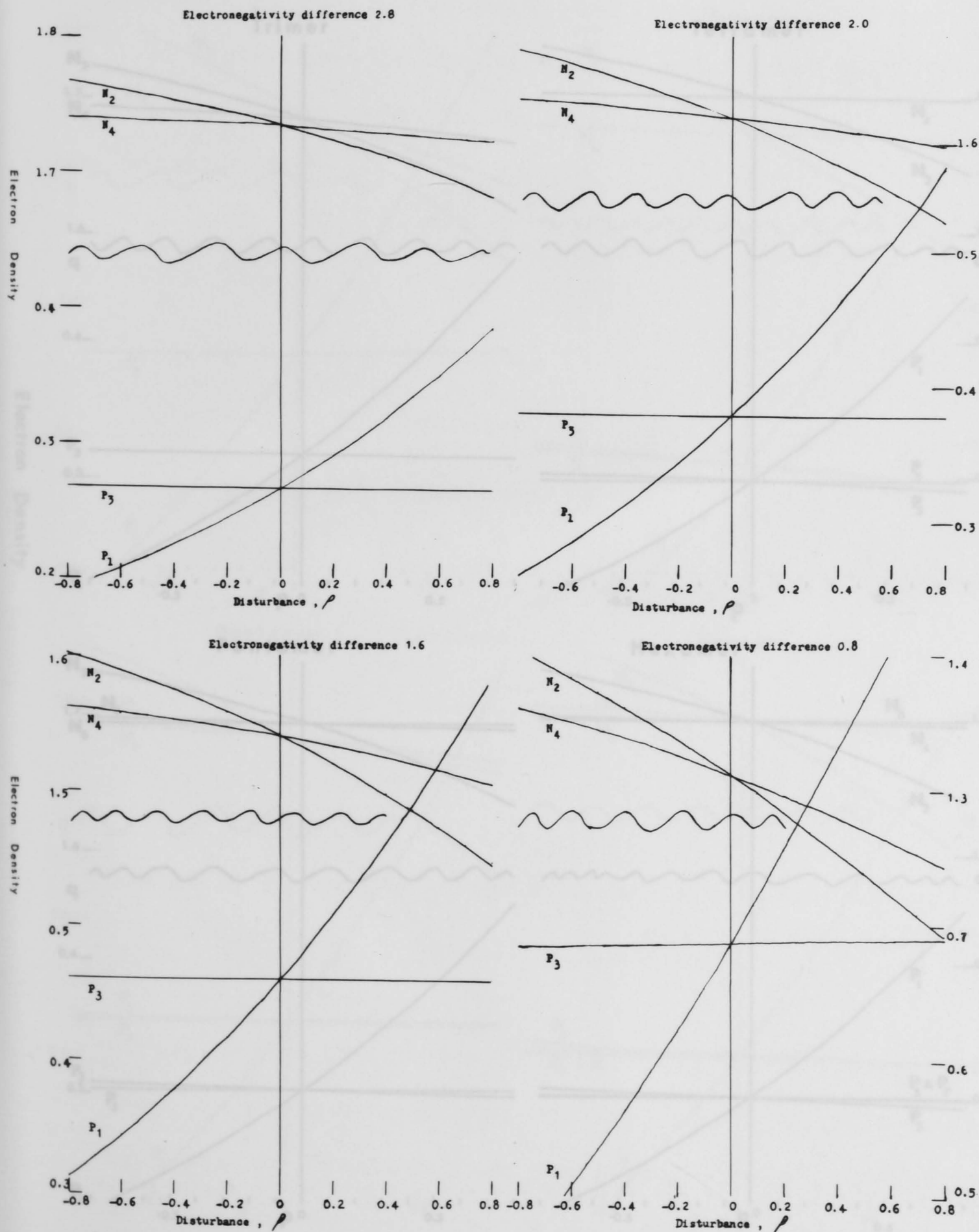
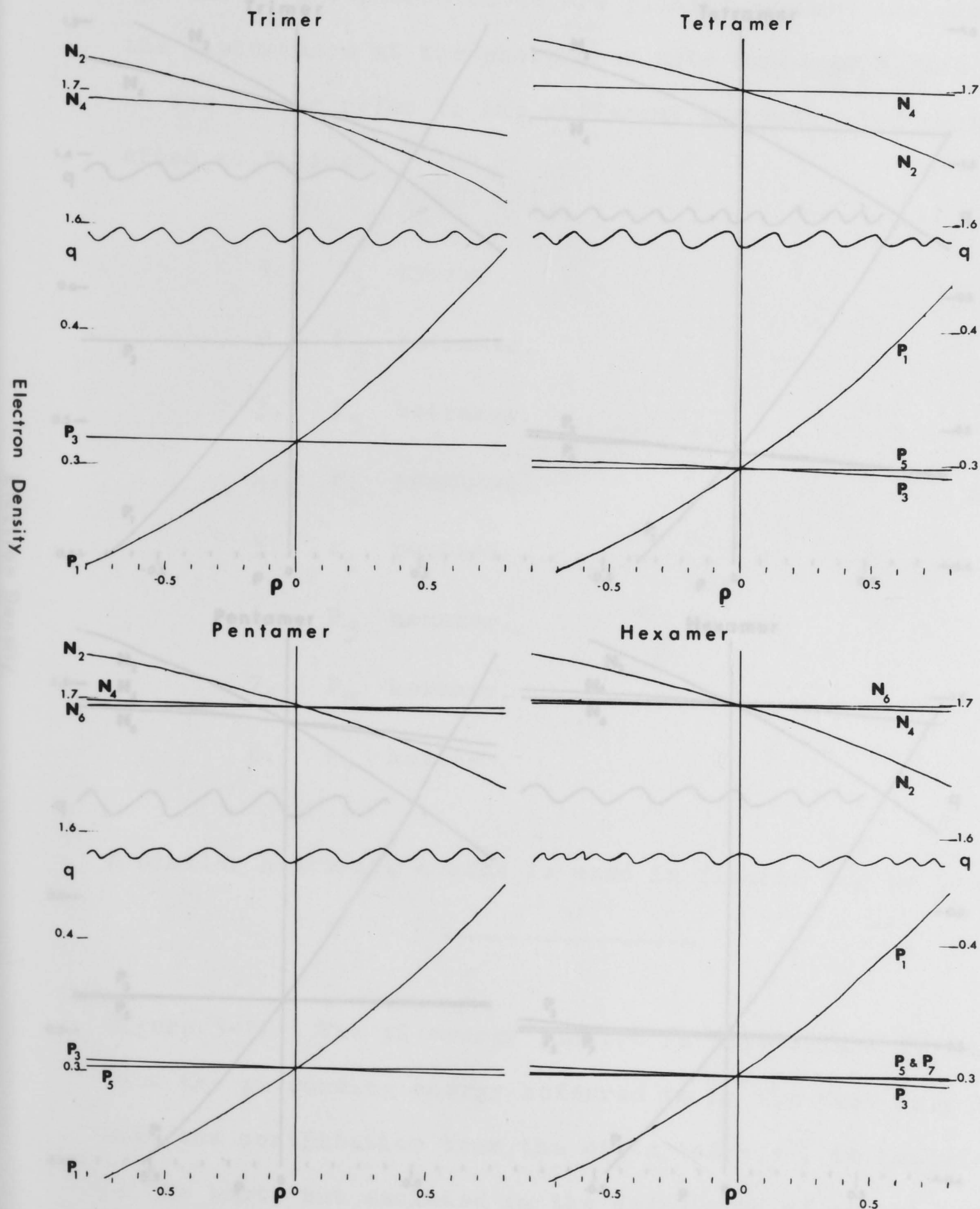


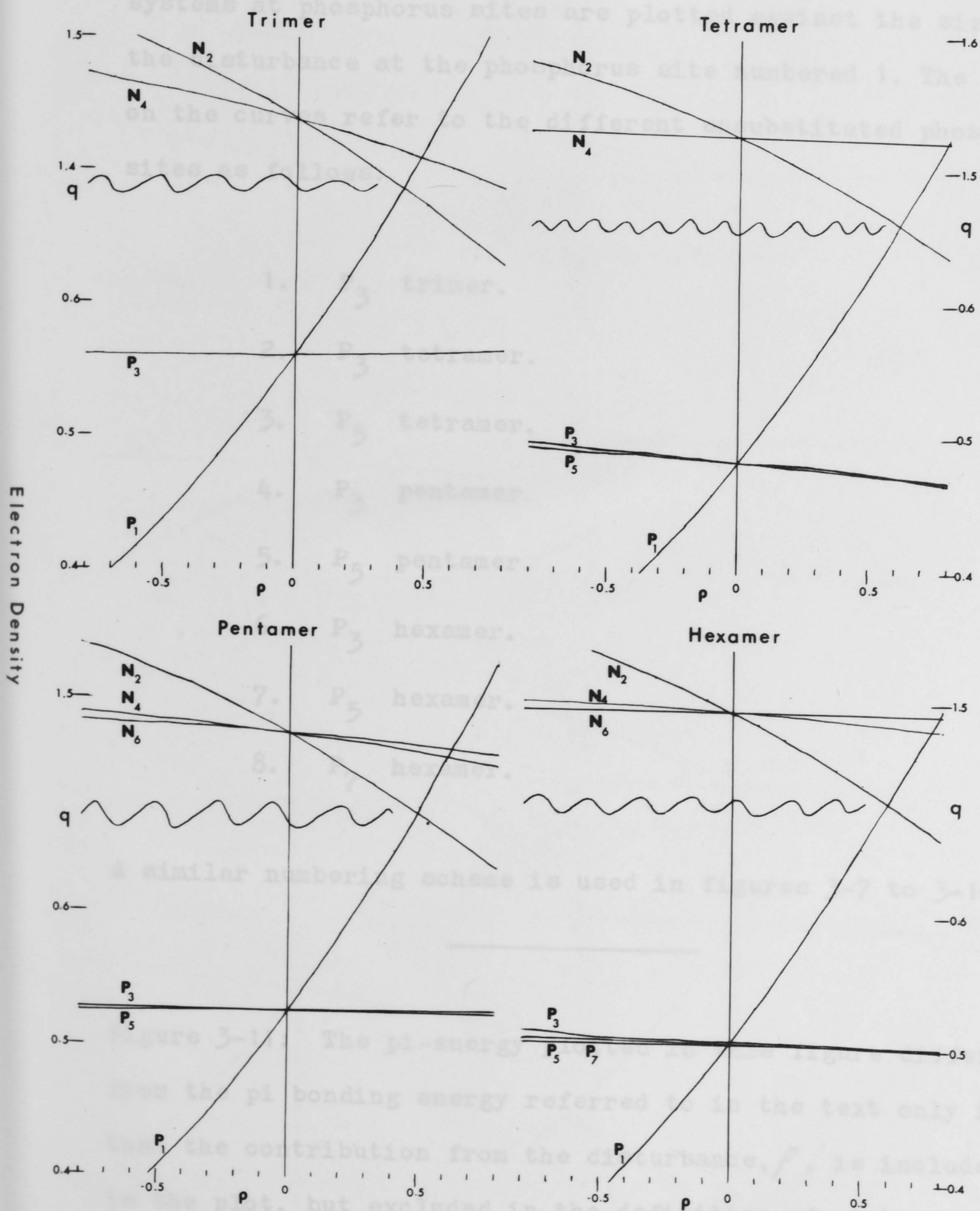
FIG. 3-2: Homomorphic Systems. $\sigma = 1.2$



KEY to figures 3-4 to 3-6:

FIG 3-3: Homomorphic Systems

$\sigma = 0.6$



KEY to figures 3-4 to 3-6:

In these figures the changes in electron density in the pi-systems at phosphorus sites are plotted against the size of the disturbance at the phosphorus site numbered 1. The numbers on the curves refer to the different unsubstituted phosphorus sites as follows:

1. P_3 trimer.
2. P_3 tetramer.
3. P_5 tetramer.
4. P_3 pentamer.
5. P_5 pentamer.
6. P_3 hexamer.
7. P_5 hexamer.
8. P_7 hexamer.

A similar numbering scheme is used in figures 3-7 to 3-10.

Figure 3-11: The pi-energy plotted in this figure differs from the pi bonding energy referred to in the text only in that the contribution from the disturbance, ρ , is included in the plot, but excluded in the definition of pi bonding energy.

FIG 3-4 Heteromorphic Systems

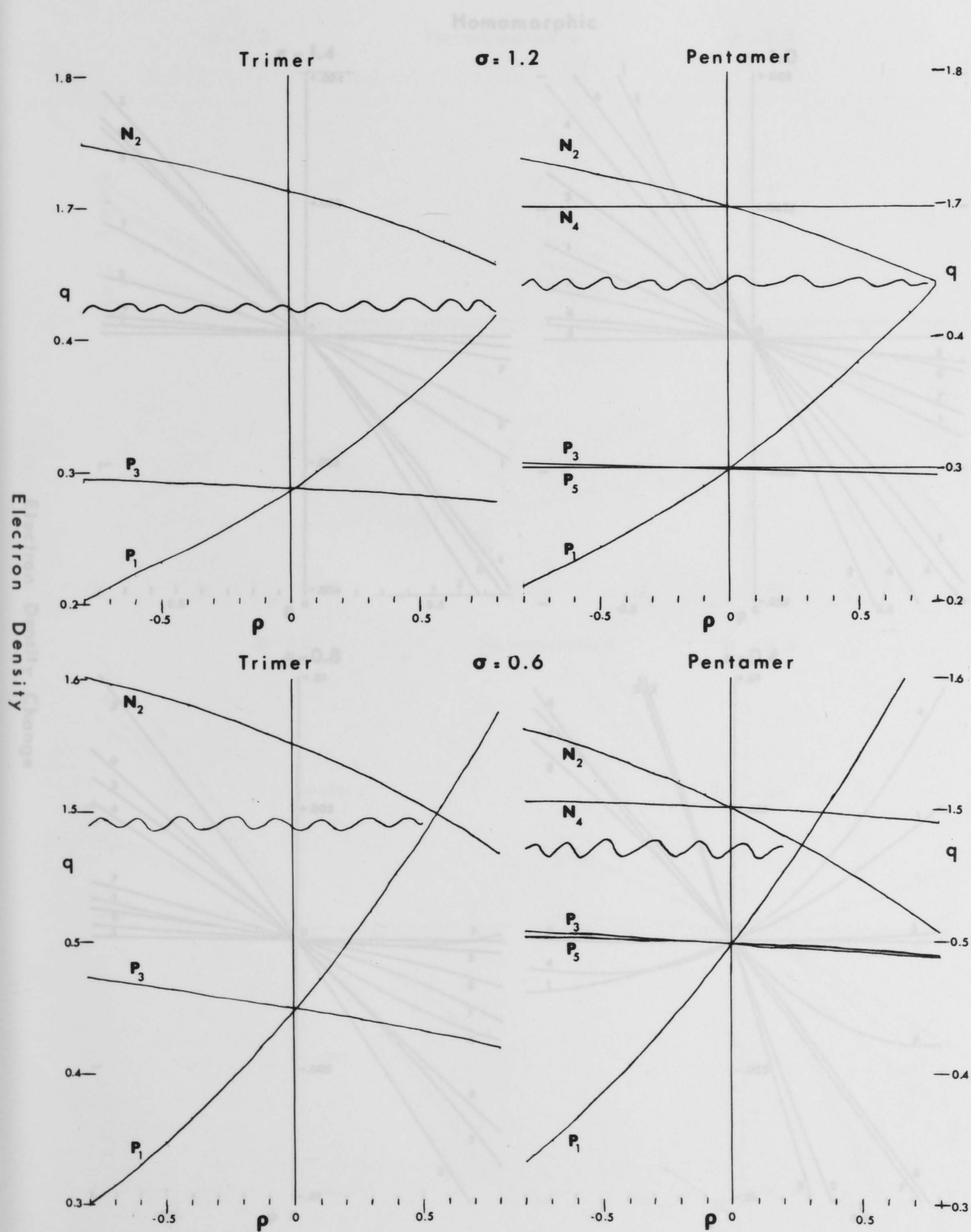


FIG 3-5: Electron Density Changes on P Sites

Electron Density Change

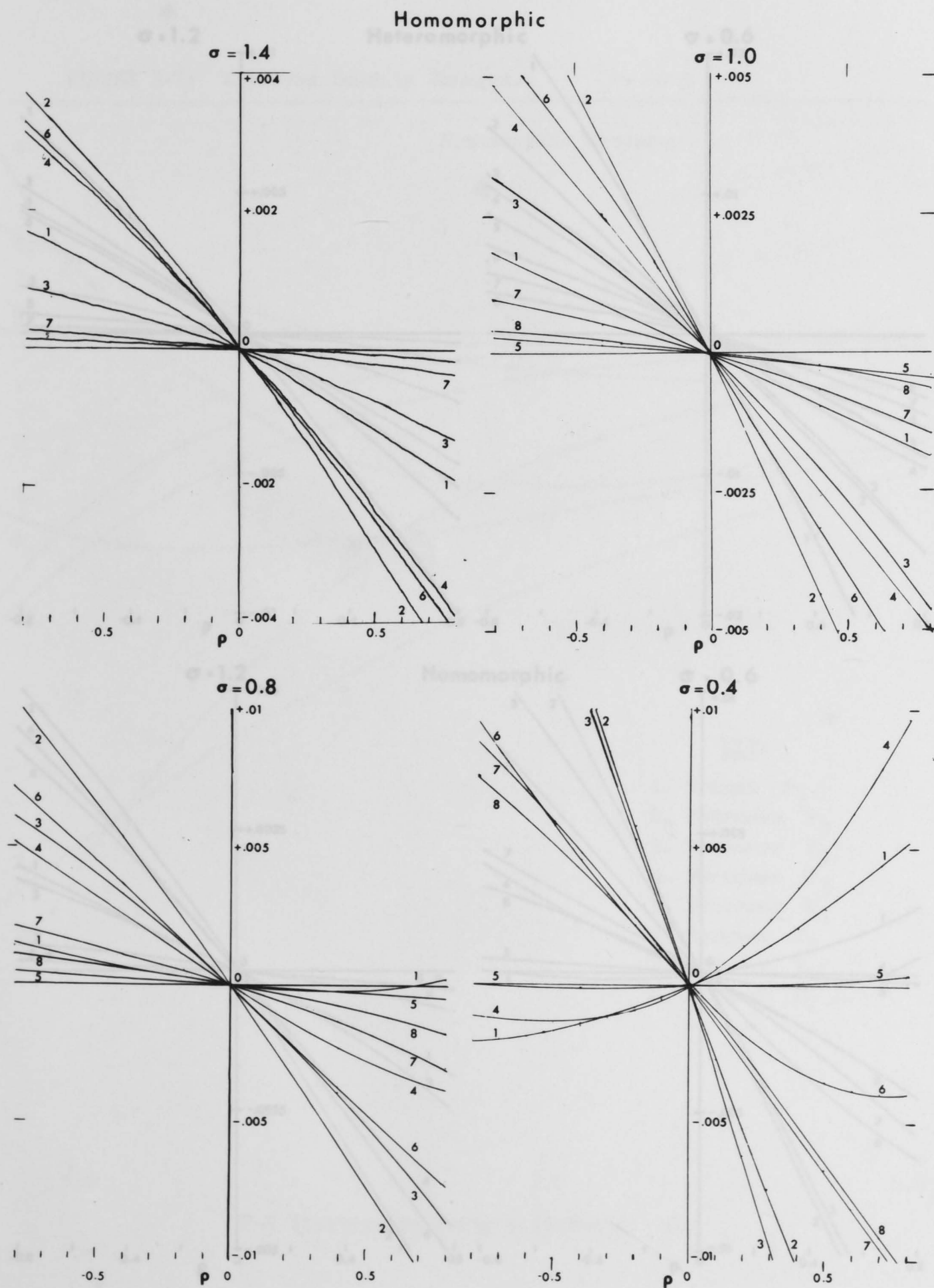


FIG 3-6: Electron Density Changes on P Sites

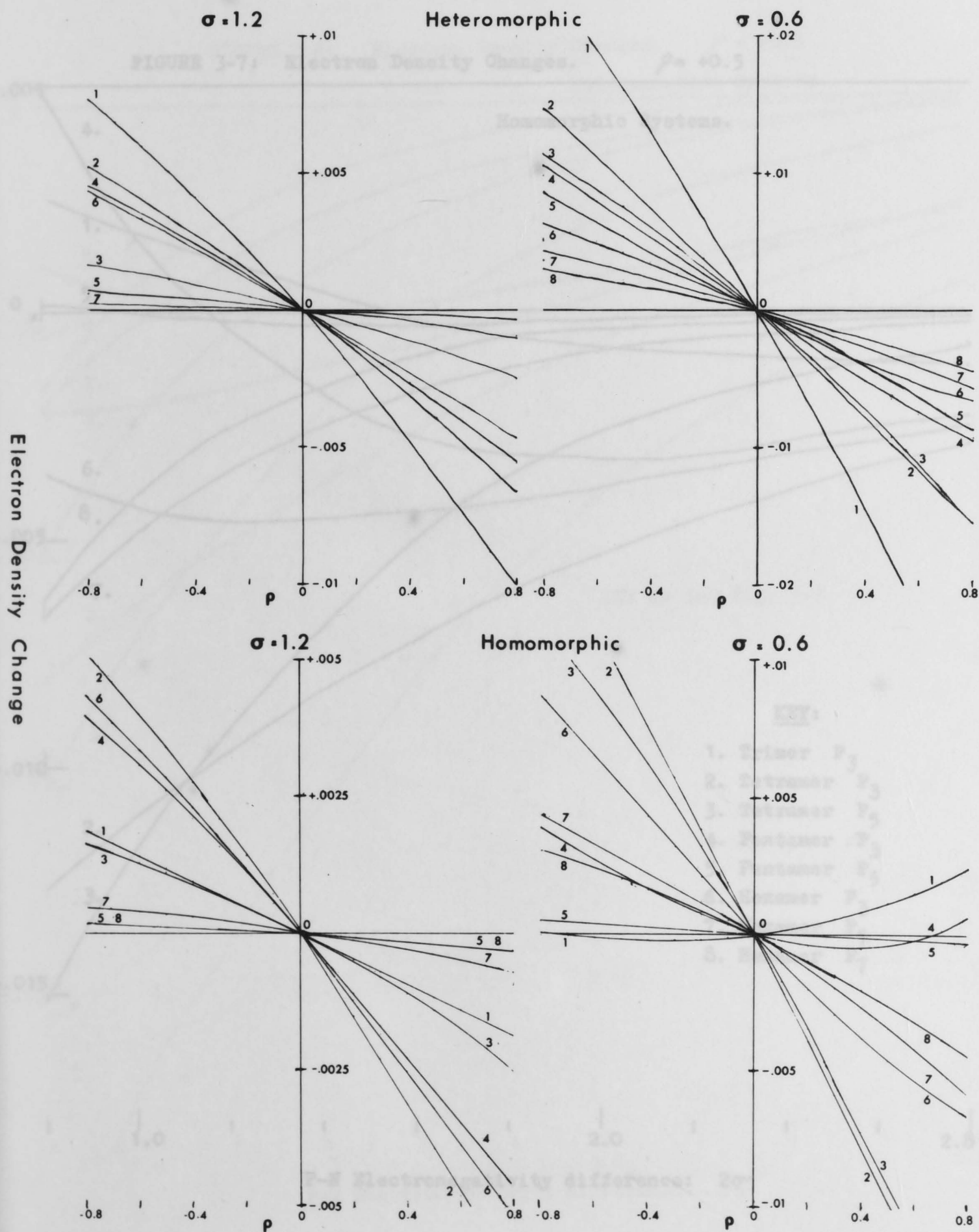


FIGURE 3-7: Electron Density Changes. $\rho = +0.5$

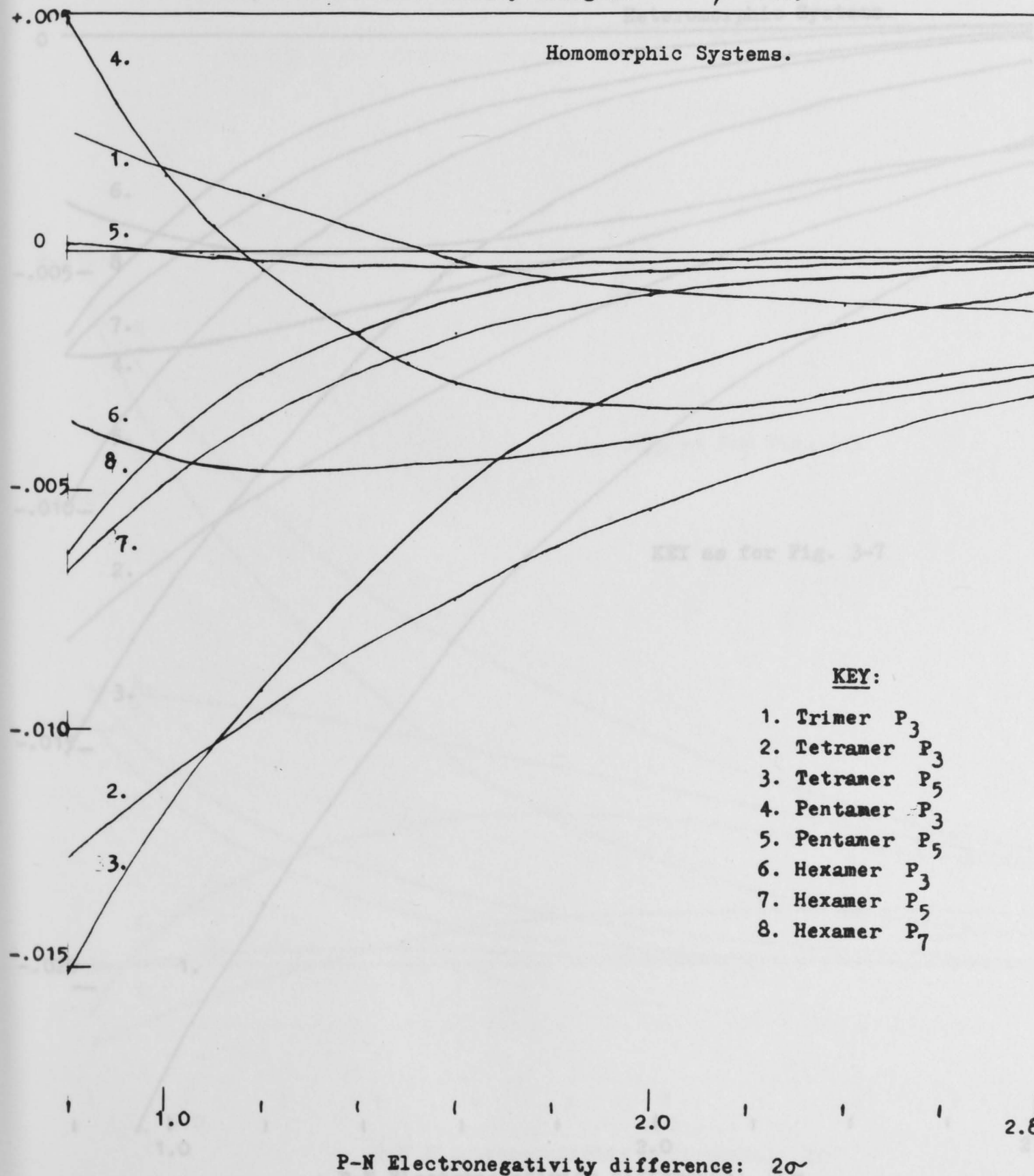
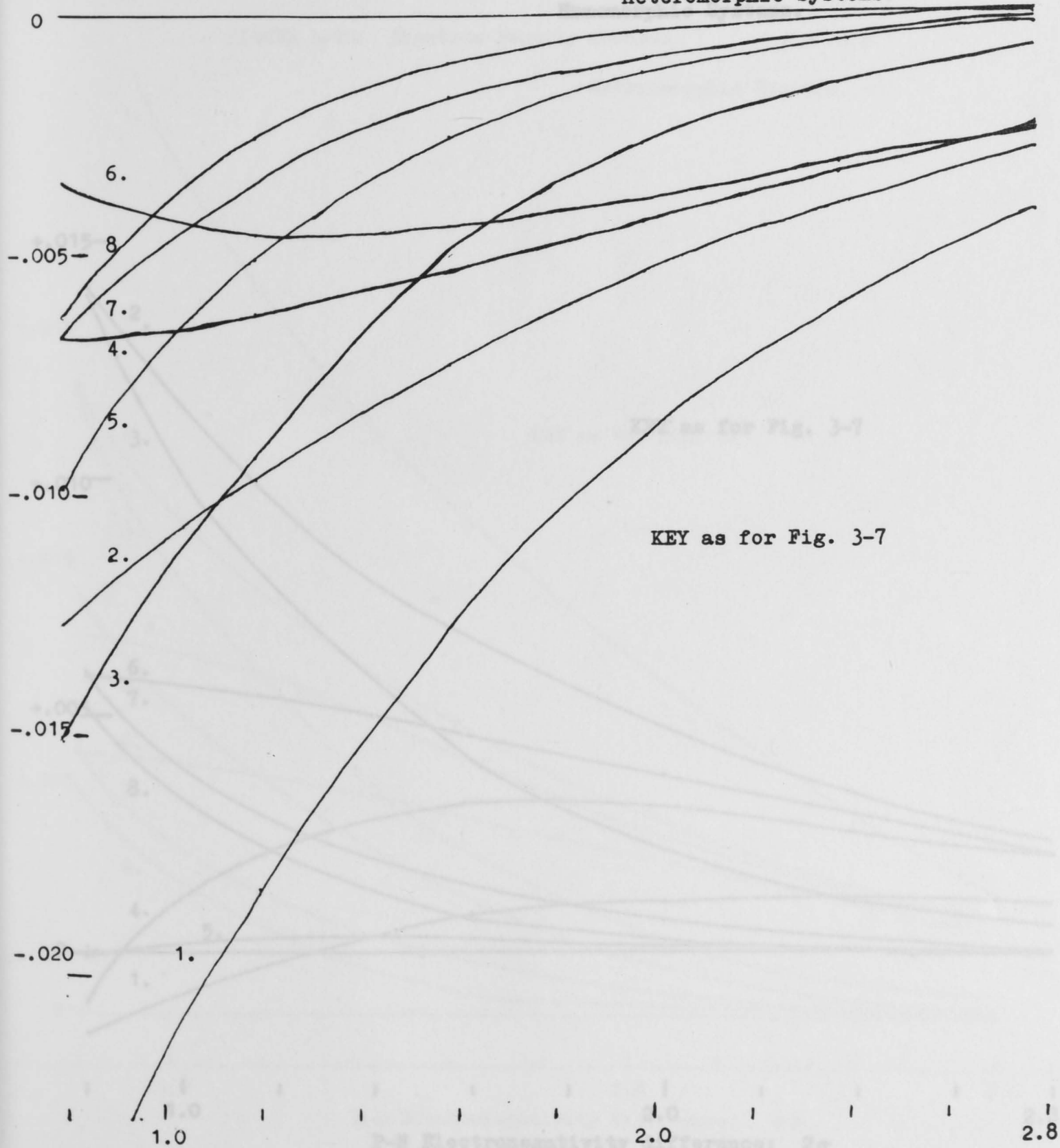


FIGURE 3-8: Electron Density Changes. $\rho = +0.5$

Heteromorphic Systems.



P-N Electronegativity difference: 2σ

FIGURE 3-9: Electron Density Changes. $\rho = -0.5$
Homomorphic Systems.

FIGURE 3-10: Electron Density Changes. $\rho = -0.5$
Heteromorphic Systems.

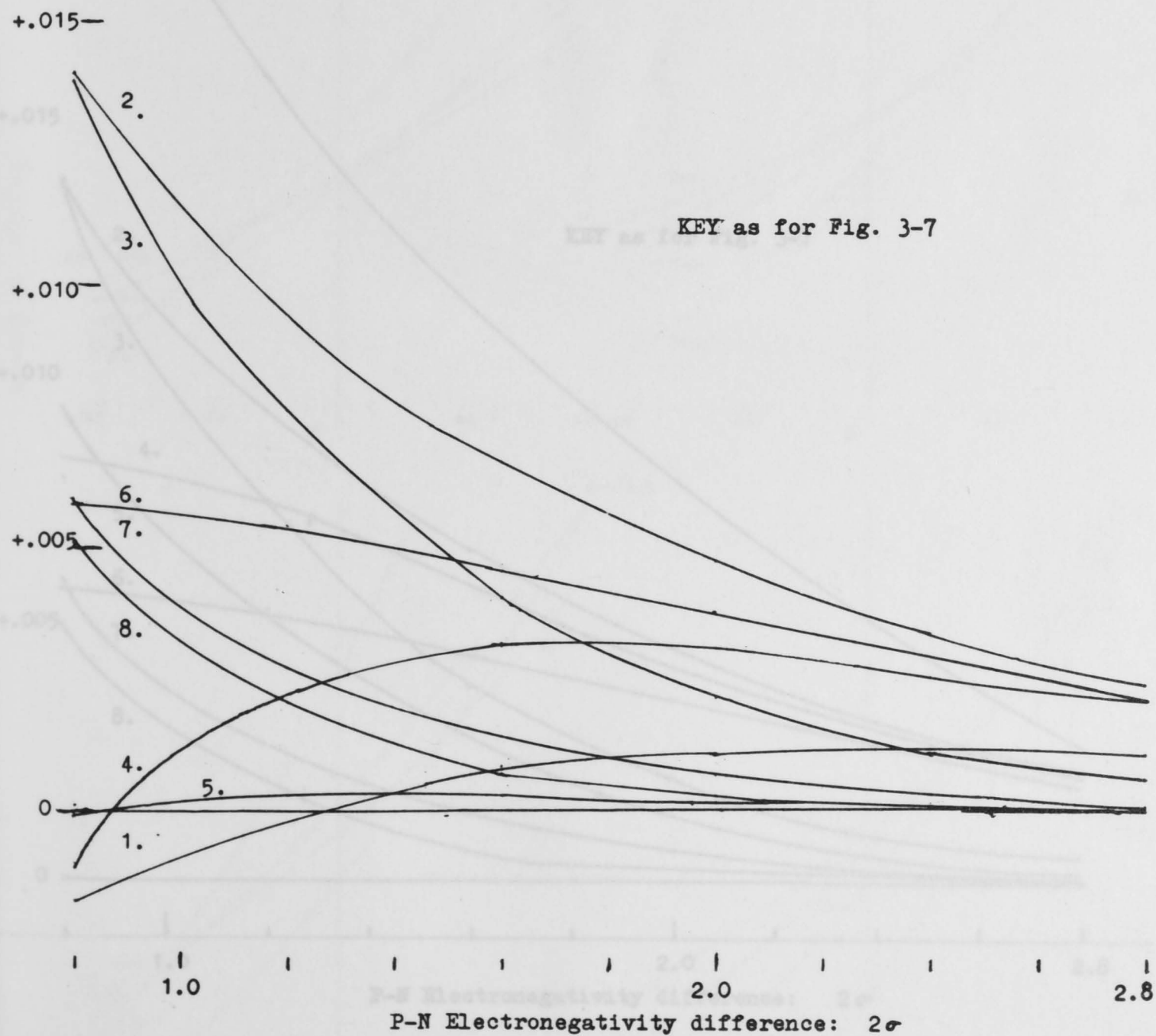


FIG 3.11: Pi Energy per (PNX₂) Unit

FIGURE 3-10: Electron Density Changes. $\rho = -0.5$

Heteromorphous Systems.

KEY as for Fig. 3-7

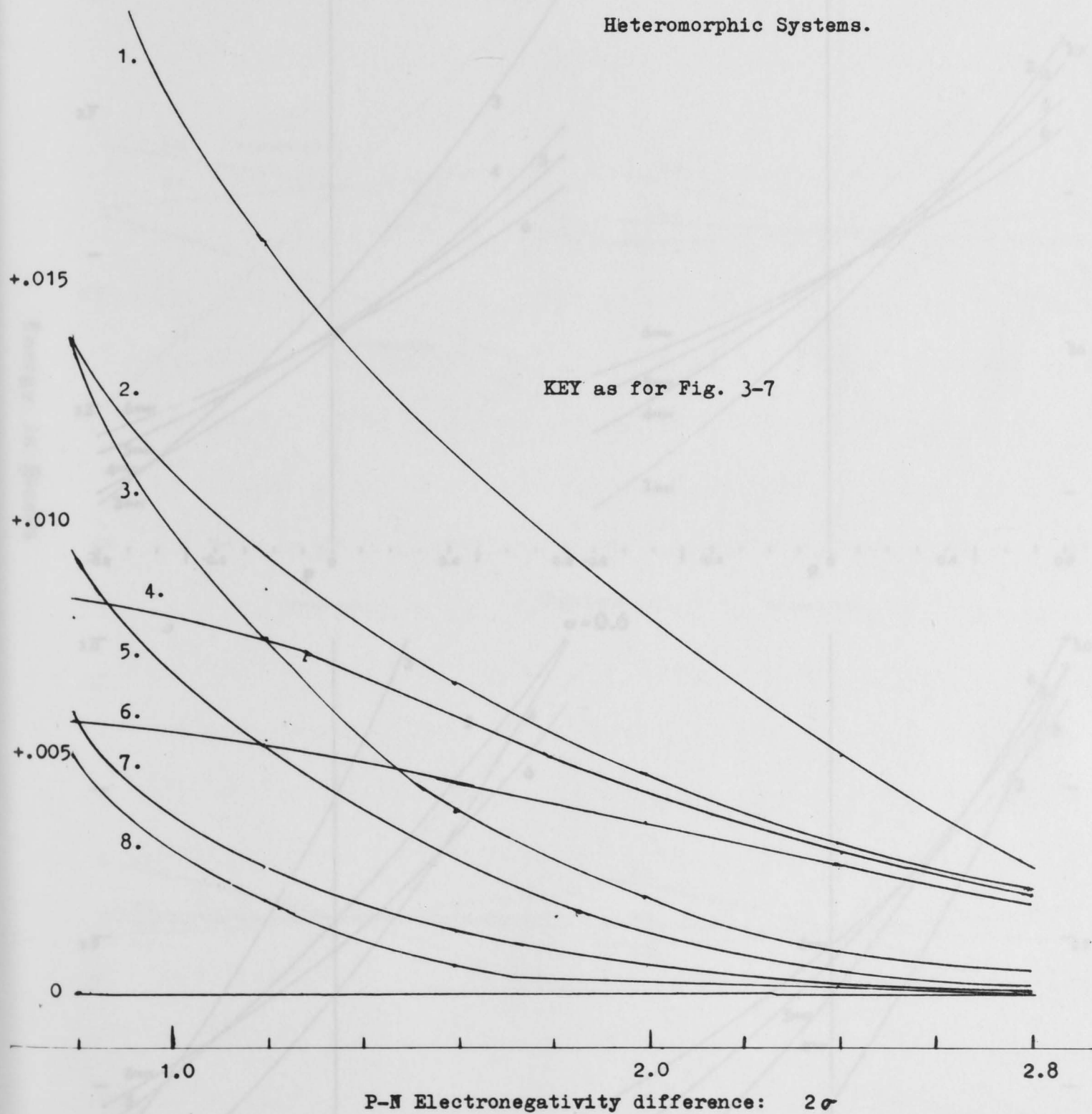


FIG 3-11: Pi Energy per (PNX₂) Unit

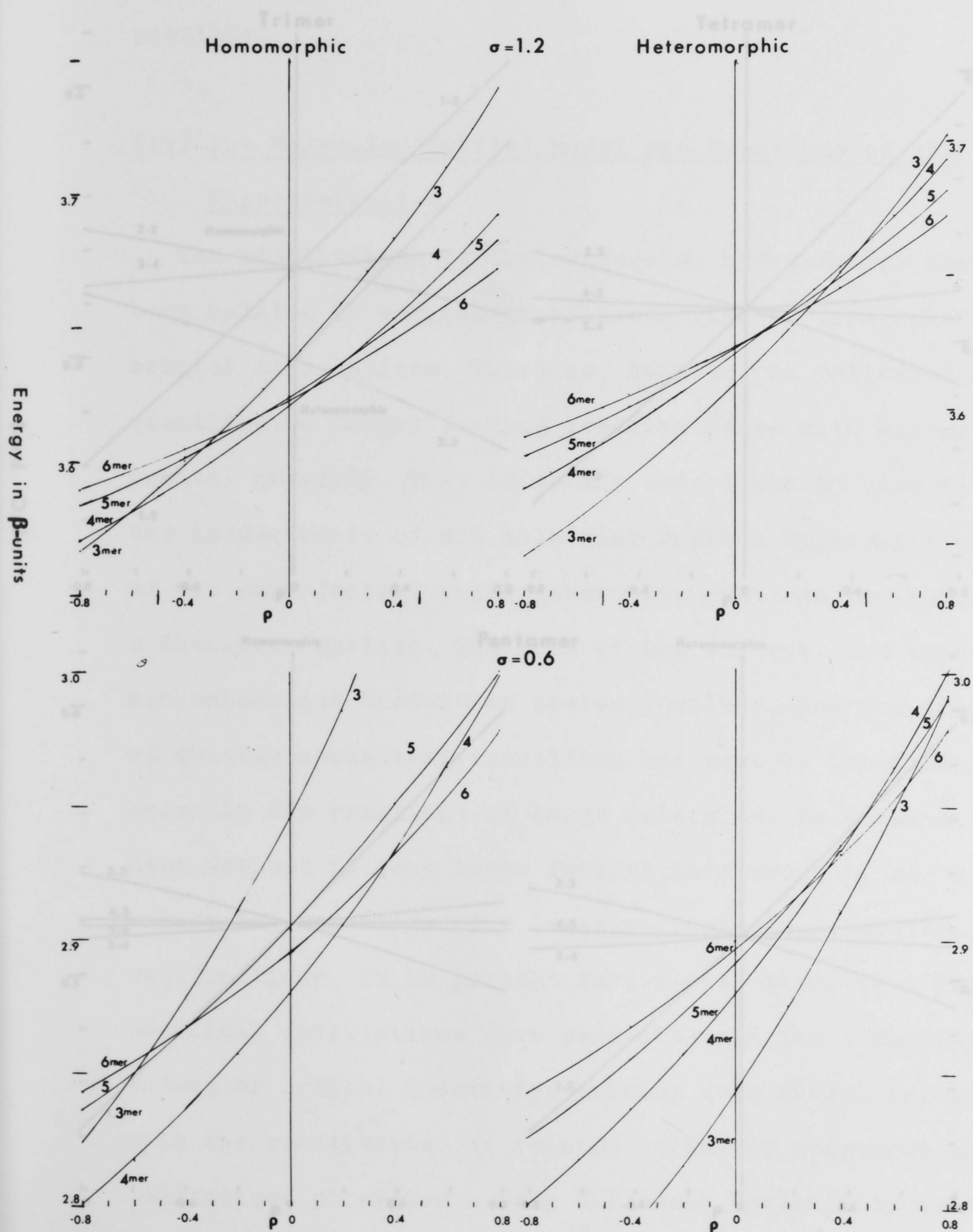
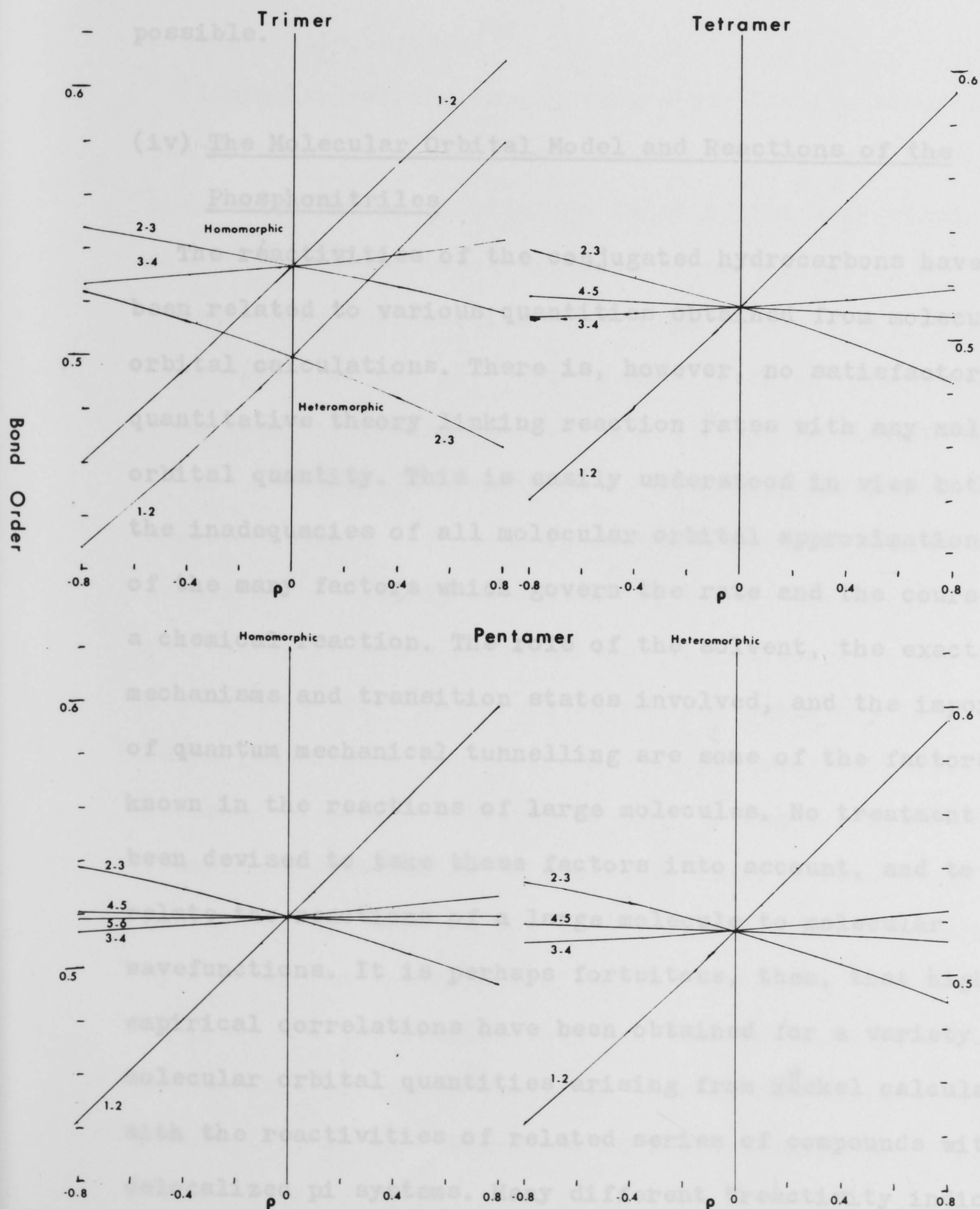


FIG 3-12: Pi Bond Orders $\sigma=1.0$



and the trace of the secular matrix. This is the energy advantage in allotting the pi electrons to the Hückel molecular orbitals, rather than allotting them one each to the basis orbitals of the system. Alternative definitions are possible.

(iv) The Molecular Orbital Model and Reactions of the Phosponitriles

The reactivities of the conjugated hydrocarbons have often been related to various quantities obtained from molecular orbital calculations. There is, however, no satisfactory quantitative theory linking reaction rates with any molecular orbital quantity. This is easily understood in view both of the inadequacies of all molecular orbital approximations and of the many factors which govern the rate and the course of a chemical reaction. The role of the solvent, the exact mechanisms and transition states involved, and the importance of quantum mechanical tunnelling are some of the factors not known in the reactions of large molecules. No treatment has been devised to take these factors into account, and to relate the reactions of a large molecule to molecular wavefunctions. It is perhaps fortuitous, then, that high empirical correlations have been obtained for a variety of molecular orbital quantities arising from Hückel calculations with the reactivities of related series of compounds with delocalized pi systems. Many different "reactivity indices"

have been proposed; most of these are closely interrelated quantities. The correlations have been extensively studied, particularly with regard to electrophilic substitution in benzene derivatives, polycyclic aromatic hydrocarbons, and nitrogen heterocycles^{1,2}.

A similar correlation, giving a qualitative account of the patterns of nucleophilic substitution characteristic of the cyclic phosphonitriles in terms of the very simple molecular orbital model explored in this chapter, is presented in this section. The index of reactivity which has been chosen is the pi electron density in the in-plane (homomorphic) system centred on the reacting phosphorus site.

The nucleophilic reactions of the phosphonitrilic compounds which have been studied all proceed by a SN_2 mechanism³⁷. Although the geometry of the transition state is not known, it seems probable that the nucleophile approaches a phosphorus site in the plane of the phosphonitrile ring. The angle between the exocyclic ligands would simultaneously increase to accommodate it, so that a trigonal bipyramidal transition state would be produced. The reaction could then proceed by the loss of one of the axial ligands, accompanied by a return to a tetrahedral configuration.

There are two reasons that the electron density in the homomorphic pi system should be closely correlated with the reactivity, if this mechanism is substantially correct. Firstly, the electron density in this pi system is so located.

that it would largely influence the electrostatic force on an incoming charged or dipolar nucleophilic species, approaching in the plane of the phosphonitrile ring. Secondly, in any Hückel type of calculation, the change in internal pi energy, dE , produced by a perturbation, βdh_Y in the coulomb integral of the basis orbital χ_Y , is given by

$$dE = q_Y \beta dh_Y$$

An incoming nucleophile may be supposed to introduce a negative perturbation βdh_Y into the coulomb integral of the $d_{x^2-y^2}$ orbital of the reacting phosphorus centre. This will cause the pi energy of the in-plane system to increase (become smaller negative). As this increase is proportional to the electron density in the basis orbital, the energy disadvantage for the pi system will be smaller, the smaller is q_Y . For this to be a valid measure of reactivity, it must be assumed that the other energy changes in forming the transition state are similar in the various systems for all phosphorus sites which carry similar substituents. The variation in the energy of activation must parallel the variation in this pi energy. Both of the effects discussed act in the same direction: a lower electron density in the $3d_{x^2-y^2}$ orbital should occur at a more reactive phosphorus centre.

For the symmetrical compounds, the electron densities in the in-plane pi system centred on phosphorus increase in the order tetramer < hexamer < pentamer << trimer. Second order

rate constants, and activation energies, obtained by Sowerby for the exchange of chloride ion with chlorophosphonitriles in acetonitrile solution⁵³, are shown in table 3-3. The rate of reaction of the hexamer is slow because its pre-exponential term is somewhat smaller than those of the other species. Otherwise the electron density correlates well, both with reaction rate, and with enthalpy of activation.

Table 3-3: Rate of Exchange of Cl^- in Acetonitrile
(from reference 53)

Compound	$k_2(25^\circ\text{C})$	ΔH^\ddagger	$q_p(3d_{x^2-y^2}), \sigma = 0.8$
$(\text{NPCl}_2)_3$	0.0501	18.3 Kcal./mole	0.460
$(\text{NPCl}_2)_4$	0.892	16.3	0.411
$(\text{NPCl}_2)_5$	0.281	17.0	0.432
$(\text{NPCl}_2)_6$	0.188	16.3	0.423

An interesting effect is found in the reaction of the chlorophosphonitriles with fluoride ion. If the trimeric compound, hexachlorophosphonitrile, is reacted with a limited amount of fluoride, a range of fluorochlorophosphonitriles is obtained. There is a strong trend favouring geminal substitution, so that of the isomeric species, geminally substituted isomers predominate, and slightly larger amounts of compounds containing an even number of fluorine substituents are produced. Apart from this effect, though, the distribution of the products is close to a statistical spread. When the same reaction is carried out for the tetrameric species, an entirely different result is obtained. The

products of the reaction are only the octafluorophosphonitrile and unreacted octachlorophosphonitrile. No significant quantities of any intermediate compound are obtained, and special conditions must be used to obtain these compounds from the reaction⁵⁴. The reaction of the pentameric species is similar to that of the tetramer, except that it is easier to obtain the intermediate species⁵¹. All of the derivatives which have been obtained from the larger systems indicate a strong preference for geminal substitution, and a preference for reaction on phosphorus sites close to PF_2 groups (e.g. reaction goes to P_3 rather than P_5 in $(\text{NPF}_2)(\text{NPCl}_2)_3$).

Some implications which may be drawn from these reactions are relevant to the comparison of molecular orbital quantities with reactivity. For the reactions to occur as outlined above it is evident that, while $(\text{NPCl}_2)_3$, $(\text{NPF}_2)(\text{NPCl}_2)_2$, and $(\text{NPF}_2)_2(\text{NPCl}_2)$ must have closely similar rates of reaction in the experimental conditions, the intermediate tetrameric species, $(\text{NPF}_2)(\text{NPCl}_2)_3$, $(\text{NPF}_2)_2(\text{NPCl}_2)_2$, and $(\text{NPF}_2)_3(\text{NPCl}_2)$ must all react much more rapidly than does $(\text{NPCl}_2)_4$. This is in accord with the trends in electron density in the in-plane π orbitals of unsubstituted phosphorus centres. Figure 3-7 shows the changes in electron density on unsubstituted phosphorus orbitals due to an increase in the electronegativity of the orbital centred on P_1 . Such a change is introduced by the replacement of a PCl_2 site with a PF_2 site. For a P-N electronegativity difference anywhere in the range

$2\sigma' = 1.2$ to 2.8 , a parallel between electron density and these reactivities occurs. A value of $2\sigma' = 1.6$ provides a good picture. Here, replacement of a PCl_2 group with a PF_2 in the trimer produces a change of only 0.0002 in the electron density on P_3 . By contrast, the electron density on P_3 in $(\text{NPF}_2)(\text{NPCl}_2)_3$ is considerably lower than that in $(\text{NPCl}_2)_4$, the difference being 0.0073 . The corresponding differences in the hexamer and the pentamer are 0.0039 and 0.0032 . In all cases the largest decrease in electron density occurs on the phosphorus site P_3 , nearest the disturbed site. Once again, the phosphorus orbitals carrying lower electron density are centred on the more reactive sites.

At a parameter value $2\sigma' = 1.2$, it can be seen from figure 3-7 that the electron density changes on phosphorus centres remote from the disturbed site become larger than those on the nearer phosphorus centres. It is doubtful, though, that this effect could be correlated to the behaviour of any phosphonitrilic compound, as it is unlikely that two different substituents could be found which would contract the phosphorus orbitals sufficiently to achieve such a low electronegativity difference from the nitrogen orbitals. As the P-N electronegativity difference increases, the differences in electron distribution between the trimer and the other species become less marked. If this trend is reproduced in the reactivities, one may expect that there would be less

tendency for intermediate, unsymmetrically substituted compounds to form in the partial fluoridation of hexabromophosphonitrile or hexa-dimethylamino-phosphonitrile.

The changes in electron density for a disturbance due to a less electronegative substituent (or an electron releasing substituent) at a phosphorus site are shown in figure 3-9. In this case the original undisturbed system always has the lowest electron density. An increase in electron density from this value leads to the inference that a reaction with a limited amount of nucleophile may proceed stepwise. This seems unlikely for the early steps in the reaction, as there are phosphorus atoms remote from the disturbance in each system which will not be greatly affected by it. After several substitutions have taken place, though, there will be no phosphorus site remote from a disturbance site, and the reactions of these species may be expected to slow somewhat. Some orientation effects which have been observed in the reactions of amines with octachlorophosphonitrile lend limited support to this view. In one case the predominant pattern of disubstitution produces the 1,5-diaminohexachlorophosphonitrile. In another, the disubstitution proceeds geminally, but the major trisubstituted product is the 1,1,5-triaminopentachlorophosphonitrile^{51,54}.

The results of simple molecular orbital treatments of the phosphonitrilic compounds appear to give a suitable description of their pi electronic structure. In addition to the

properties of the substances which have previously been examined from this point of view^{37,43}, extension of the model to unsymmetrically substituted compounds gives a good qualitative correlation with the nucleophilic reactions of these substances, using models similar to those which have been used in correlating molecular orbital quantities with the electrophilic reactions characteristic of aromatic carbon compounds.

(v) Other Properties and the Molecular Orbital Model

The difficulty which arises in correlating other properties of the phosphonitrilic compounds with quantities from molecular orbital treatments, is that most of these properties are affected by the structure of both of the pi systems in the molecule, often with a different weighting. Ionization potentials are related to the energy levels of the more weakly bound pi system, and do show an alternation similar to the alternation of the energy levels in the homomorphic systems^{37,55}. Bond lengths and bond energies depend on both pi systems with a weighting determined by the relative magnitudes of β and β' . The variation observed in the different systems appears to be determined mainly by the heteromorphic pi system, with the homomorphic system exerting a secondary influence^{43,56}. The angle at the nitrogen atoms appears to be governed to some extent by the electron density in the lone pair orbital in the in-plane pi system^{43,46}.

Phosphorus chemical shifts have been reported³⁸. These quantities should depend equally on the π electron density in both systems, although other factors, such as non-planarity, may be important. A reasonable fit is obtained for the choice of parameters $\sigma = 0.6$, $\sigma' = 1.2$ to describe the π systems. A wide range of different results could also have been accounted for by using different parameter values, however.

Most of the properties which have been compared with π electron calculations have been concerned with the symmetrically substituted phosphonitriles. Unsymmetrically substituted phosphonitriles have not received the same attention, and only in isolated instances are their properties recorded. The simple molecular orbital models which have been described in this chapter should undergo more thorough testing, and probably have more useful predictions and explanations to contribute as the properties of these compounds are more thoroughly studied.

CHAPTER 4: RADIATIONLESS TRANSITIONS IN LARGE MOLECULES

(i) The Born-Oppenheimer Approximation

Ideally, a theoretical treatment of the properties of large molecules should commence with the solution of the Schrödinger equation for these systems. In practice, however, the systems are of such complexity that exact solution is not feasible. It is therefore necessary to find a suitable model which will give a good approximation to the correct solutions, as well as a physical insight into their nature. The Born-Oppenheimer, or adiabatic approximation is one feature which is common to most model treatments of large molecular systems. The Born-Oppenheimer approximation consists in describing molecular wavefunctions in products of electronic and vibrational parts. The term "adiabatic approximation" is used for the most general and accurate method of obtaining the separated wavefunctions. The "harmonic approximation" is a lower order approximation involving separated wavefunctions which is often used. It can be obtained by neglecting the third and higher terms in the fourth root of the mass ratio in the Born-Oppenheimer treatment, or by not allowing the electronic wavefunctions to vary with changing nuclear coordinates in the Born expansion⁵⁷⁻⁵⁹.

In most chemical problems, the features of a large molecule which are important are the distribution and the motion of the electrons and the nuclei in the molecule. Because of the large

differences in mass between electrons and nuclei, the electronic and nuclear properties have very different descriptions. Electronic states are typically separated by large energy intervals, and position-momentum uncertainty requirements preclude any understanding of electron position or motion in a classical picture. The nuclear motions, on the other hand, are comparatively slow and well-defined, and semiclassical models are common in problems related to molecular vibrations. There are thus reasons, beyond the obvious simplification, for seeking a model which separates the electronic and nuclear problems. In the original paper by Born and Oppenheimer⁵⁷ the Schrödinger equation is solved by a power series expansion in the fourth root of the ratio of electron mass to nuclear mass. Neglect of terms beyond the fourth order leads to solutions which can be separated into electronic and nuclear parts. A later treatment by Born^{58,59} showed that one of the correction terms could be incorporated into the potential governing nuclear configuration, and was able to produce a slightly improved separable wavefunction. The latter treatment is outlined here.

A suitable Hamiltonian to describe the electronic and nuclear structure of a large molecule is

$$H = T_{el} + T_{nu} + V(Q, q) \quad (1)$$

where T_{el} is the electronic kinetic energy operator, T_{nu} is the nuclear kinetic energy operator, and V is the potential where the electronic coordinates are given by the generalized

vector \underline{q} , and the nuclear coordinates are given by \underline{Q} . The complete set of "electronic" solutions $\phi_j(\underline{q})$ is known for a general nuclear configuration \underline{Q} which is fixed.

$$[T_{el} + V(\underline{q})]\phi_j(\underline{q}) = E_j \phi_j(\underline{q}) \quad (2)$$

where V , E , and ϕ all depend parametrically on \underline{Q} . Then the exact solutions of the wave equation may be expanded in the form:

$$\Psi_i(\underline{q}, \underline{Q}) = \sum_j \chi_{ji}(\underline{Q}) \phi_j(\underline{q}, \underline{Q}) \quad (3)$$

$$\text{where } H \Psi_i(\underline{q}, \underline{Q}) = \epsilon_i \Psi_i(\underline{q}, \underline{Q}) \quad (4)$$

Substituting in (4) the expression in (3) for Ψ , and that in (1) for H , and using the result in equation (2)

$$\begin{aligned} \sum_j [T_{nu} \chi_{ji}(\underline{Q}) \phi_j(\underline{q}, \underline{Q}) + E_j(\underline{Q}) \chi_{ji}(\underline{Q}) \phi_j(\underline{q}, \underline{Q})] \\ = \epsilon_i \sum_j [\chi_{ji}(\underline{Q}) \phi_j(\underline{q}, \underline{Q})] \end{aligned} \quad (5)$$

Multiplying through by $\phi_k^*(\underline{q}, \underline{Q})$ and integrating over \underline{q} space

$$\sum_j \int \phi_k^*(\underline{q}, \underline{Q}) T_{nu} \chi_{ji}(\underline{Q}) \phi_j(\underline{q}, \underline{Q}) d\underline{q} + E_k(\underline{Q}) \chi_{ki}(\underline{Q}) = \epsilon_i \chi_{ki}(\underline{Q}) \quad (6)$$

The operator T_{nu} is given by $\sum_Y \hbar^2/2m_Y \cdot \nabla_Y^2$, where the sum ranges over all nuclei, Y , in the molecule. Expression (6) reduces to

$$\begin{aligned} T_{nu} \chi_{ki}(\underline{Q}) + \chi_{ki}(\underline{Q}) \int \phi_k^* T_{nu} \phi_j d\underline{q} + E_k(\underline{Q}) \chi_{ki}(\underline{Q}) - \epsilon_i \chi_{ki}(\underline{Q}) \\ = \sum_{j \neq k} \sum_Y \hbar^2/2m_Y \cdot [2 \text{grad}_Y \chi_{ji}(\underline{Q}) \cdot \int \phi_k^* \text{grad}_Y \phi_j d\underline{q} + \\ \chi_{ji}(\underline{Q}) \int \phi_k^* \nabla_Y^2 \phi_j d\underline{q}] \end{aligned} \quad (7)$$

The terms on the right in (7) may, for many purposes, be considered negligibly small. If this approximation is made,

then χ_{ki} and ϵ_i may be evaluated from a single uncoupled equation. χ_{ki} is necessarily zero except for a single value of k , unless ϵ_i is an eigenvalue of the equation for more than one electronic state. Even in this degenerate situation, χ_{ki} can be chosen to be non-zero for only a single value of k . Thus the approximate eigenfunctions given by this approximation may be represented as product functions.

$$\psi_i^0(Q, q) = \chi_{ki}^0(Q) \phi_k(Q, q)$$

where χ_{ki}^0 is given by

$$[T_{nu} + \int \phi_k^* T_{nu} \phi_k dq + E_k(Q)] \chi_{ki}^0 = \epsilon_i^0 \chi_{ki}^0 \quad (8)$$

A particular state ψ_i^0 may thus be regarded as belonging to the vibrational manifold of one particular electronic state ϕ_k , namely, the single state for which χ_{ki} is non-zero. This approximation thus succeeds in separating the wavefunctions to describe electronic and nuclear configurations. The electronic wavefunctions, ϕ , are correct for stationary nuclei, and depend parametrically on the nuclear coordinates. The nuclear wavefunctions are approximate, and use as a potential the expectation value of the total energy in a particular electronic state for stationary nuclei. The correction terms are clearly shown in equation (7), and their importance may be assessed in a consideration of a particular problem.

(ii) Radiationless Decay of Electronically Excited States

When a molecular system absorbs visible or ultraviolet radiation, it is excited into one of the vibrational levels of a higher electronic state. The energy of the photon absorbed is transformed into electronic and vibrational energy of the system. If the radiation field were the only perturbation which affected the system, relaxation could occur only through photon creation, and the observation which could be expected would be fluorescence with a quantum yield of unity. In practice, however, the observation is quite different. In large molecular systems, the higher electronic states do not fluoresce. In many cases the first excited singlet electronic state does fluoresce, but the yield of the fluorescence is generally much less than unity. The experimental observations for different types of systems, and for different phases, are reviewed by Seybold and Gouterman⁶⁰.

Clearly, there must be perturbations other than the radiation field which operate on the molecular excited state to produce dissipation of the molecular energy at a rate which is at least comparable with, and usually faster than the rate of photon emission. In fluid phases, the main interactions which affect the isolated molecule wavefunctions are intermolecular collisions, while in the solid state intermolecular coupling can occur through phonon interactions. These types of interaction allow transfer of energy from the

molecule to its environment at a fast rate, and therefore compete with photon emission in reducing the concentration of electronically excited molecules.

In 1963, Gouterman⁶¹ presented a treatment of radiationless relaxation of an electronically excited guest molecule in a dilute mixed crystal. The treatment was based on the coupling of the molecular states to the states of the phonon field, which was treated analogously to the radiative problem, where molecular states are coupled to the photon field. The method is largely parametric, and subsequent experimental results⁶² have shown that the temperature dependence predicted by the theory does not apply, and that the value which must be ascribed to one of the matrix elements in the theory to fit the observed rates is improbably high.

Robinson and Frosch^{63,64} used a different approach. They considered the intramolecular relaxation of electronic energy that could arise because of the correction terms in the Born-Oppenheimer approximation as well as the dissipative relaxation due to intermolecular interactions. Their model envisaged the system originally prepared by photon absorption in a non-stationary state of the molecular Hamiltonian (the term "molecular Hamiltonian" in this chapter refers to the exact Hamiltonian of the isolated molecular system, without the inclusion of off-diagonal terms arising from interaction of the molecule with the radiation field). This state resonates with other states

having lower electronic energy and higher vibrational energy, due to the coupling of nuclear and electronic motion described by the correction terms in the Born-Oppenheimer approximation; it is assumed that the initial state after photon absorption is effectively a Born-Oppenheimer state. Vibrational relaxation of the states with high vibrational energy is supposed to occur through intermolecular interactions, and to be fast compared with the intramolecular electronic relaxation. The treatment of the various processes is largely empirical.

Hunt, McCoy and Ross⁶⁵ envisaged a similar type of mechanism for the radiationless decay, but used a slightly different viewpoint in obtaining the rates. They considered the vibrational potential surfaces of the different electronic states, and suggested that the factor which governs the rate of the slower radiationless processes, at least, is the width of the potential barrier, if any, between the initial state (a Born-Oppenheimer state), and the vibrational states of the lower electronic manifold which are quasi-degenerate with it. An excellent correlation was found between the rates of radiationless processes in different aromatic hydrocarbons, and the barrier widths between approximate potential surfaces at the zero vibrational level of the upper electronic state. The surfaces were obtained from excited state geometries calculated by McCoy and Ross⁶⁶, and consider only the distortions and origin displacements in

the modes showing the most prominent spectral progressions. The potential barrier widths are closely related to the vibrational overlap functions which play an important part in the treatment of Robinson and Frosch.

In a recent series of papers, Siebrand⁶⁷⁻⁷⁰ used essentially the Robinson and Frosch model, and undertook a more detailed examination of the vibrational overlap functions. He derived more accurate expressions for these, and was able to offer an explanation of the isotope effects in the various types of radiationless transitions, and to compare the rates for series of closely related compounds.

An alternative mechanism, which was originally proposed by Sponer and Teller⁷¹, and recently revived in a paper by Ting⁷², is to suppose that the perturbation term which leads to radiationless transitions is the second order term for the interaction of the radiation field with the system. Emission and reabsorption of a virtual photon can take the system from a state into a different state of the same energy. There are, however, serious errors in Ting's formalism, and there is reason to believe that this term would be many orders of magnitude too small to account for the observed rates of radiationless transitions.⁷³

Lin⁷⁴ examines the problem from a theoretical viewpoint in a model which is formally similar to that of Robinson and Frosch, and derives a series of complex quantum mechanical expressions, without recourse to the empirical

simplification characteristic of the other treatments. From these expressions he is able to offer a qualitative explanation of several features of radiationless transitions.

One of the more complete recent treatments of the problem is that of Bixon and Jortner⁷⁵. They devise a simple model, in which an initial state is coupled to a series of evenly spaced final states by a set of identical perturbation matrix elements. They obtain expressions for level shifts, effective linewidth of the initial state, and the rate of decay of the initial state. They then consider the properties of a conventional light source, and show that the state of a molecular system produced by photon absorption is not necessarily a stationary state of the molecular Hamiltonian. In many practical situations the state approximates very closely to a Born-Oppenheimer state. In such cases, the Born-Oppenheimer wavefunctions form a convenient zero order basis set, and the difference between the Born-Oppenheimer Hamiltonian and the molecular Hamiltonian is the perturbation which leads to intramolecular relaxation of the initial Born-Oppenheimer state.

(iii) Radiationless Decay in Dilute Gases

As most of the theories described in the previous section ascribe some role to the molecular environment, the effects of different environments on the rates of radiationless transitions are experimental observables which should be

described to some effect by the various theories, and which may distinguish between them. In particular, experiments carried out in the low pressure gas phase are critical, because in this situation the environment is continuously variable, and in the limit of low pressures, absorption and luminescence may be studied in the effective absence of an environment. The criterion for this condition is that the collision time should be much longer than the overall lifetime of the state being observed, and this is a practical possibility for observations on all but the lowest triplet state in the typical aromatic hydrocarbon.

Several experiments of this type have been performed. When naphthalene⁷⁶, anthracene^{77,78}, and tetracene⁷⁹ are excited into their second singlet electronic states by absorption of an appropriate frequency from a mercury arc, the observation at very low gas pressures is that the fluorescence spectrum is very similar to that of the first excited singlet, but somewhat more diffuse, and slightly shifted to the red. No luminescence whatsoever could be detected in the shorter wavelength region where second singlet to ground state fluorescence would have been expected, nor was any near-infrared luminescence detected, corresponding to second singlet to first singlet radiative transitions.

Benzene fluorescence has been found to have a constant quantum yield, significantly less than unity, at low gas

pressures⁸⁰. Moreover, cis-butene is isomerized to trans-butene when low pressures of benzene and cis-butene vapours are irradiated together. This isomerization of cis-butene is characteristic of the triplet state of benzene, and has never been observed to occur with singlet benzene. No isomerization was produced when cis-butene was irradiated in the absence of benzene under similar conditions. The collision times at the pressures used ranged from much shorter than the lifetime of the benzene first singlet state to considerably longer than this lifetime. The triplet lifetime is much longer. In the experiments on naphthalene, anthracene, and tetracene, collision times were considerably longer than the lifetimes of the second singlet states.

Several inferences may be drawn from these results. The first is that observations similar to those which are described as radiationless transitions are made even when the experiments are performed in the absence of a dissipative molecular environment. A theory must explain how these processes can occur efficiently without reliance on environmental perturbations. The small changes in quantum yield of fluorescence with changing gas pressure require that the main rate-controlling step be an intramolecular process, at least in the intersystem crossing of benzene.

Environmental perturbations are essential to Gouterman's theory, and also play an important part in the mechanisms envisaged by Robinson and Frosch, Hunt, McCoy and Ross,

and Lin. However, as pointed out by Bixon and Jortner, the environment is not essential to the type of intramolecular process which takes place in the Robinson and Frosch theory. In sufficiently large molecules the density of accessible final states with high vibrational energy and lower electronic energy is sufficient to ensure that the electronic relaxation of the state initially produced is effectively an irreversible process, rather than an oscillatory one.

Another important point is the close similarity between the emission observed in the low pressure gases and the normally observed emission of the first excited singlet state from a thermal distribution of vibrational levels. The implication is that most of the excess vibrational energy in the states which emit in the dilute gas phase experiments must be stored in modes which have no origin displacement and only a small distortion in their potential surfaces between the ground state and the first excited singlet. There is a fairly strong selection rule favouring zero quantum number change on emission in these modes. Most of the emission must originate from the zero quantum number level of the modes which appear prominently in progressions in the spectrum. If a significant amount of emission originated from the higher quantum number levels of these modes, there would be a different profile in the emission spectrum, as well as a noticeable extension of the spectrum to shorter wavelengths to accommodate emissions involving a

quantum number decrease in these modes. This is an important point, because in the treatment of Siebrand⁶⁸, modes which are displaced and modes which have large distortions between two electronic states play the main part in determining rates of radiationless transitions between those states. The observation is not, however, in any way inconsistent with Siebrand's treatment, as will be pointed out in a later section.

(iv) Intramolecular Relaxation of Electronically Excited States

In this section, the intramolecular relaxation process is described in terms of the supposition that the molecule is initially prepared in a non-stationary state of the molecular Hamiltonian immediately following photon absorption. The treatment follows that of Bixon and Jortner⁷⁵, with some minor modifications. An attempt has been made to include more general forms for some of their results.

Consider a set of zero-order states in an energy neighbourhood. One state, ψ_1 , is that produced by a photon absorption. A manifold of final states, $\{\psi_f\}$, mutually orthogonal, interact with the state ψ_1 under the correct molecular Hamiltonian

$$\tilde{H}^0 \psi_1 = E_1 \psi_1 ; \quad \tilde{H}^0 \psi_f = E_f \psi_f$$

$$\tilde{H} = \tilde{H}^0 + \tilde{H}'$$

$$\langle \psi_1 | \tilde{H}' | \psi_1 \rangle = \langle \psi_f | \tilde{H}' | \psi_f \rangle = 0 ; \quad \langle \psi_1 | \tilde{H}' | \psi_f \rangle = H'_{1f}$$

The stationary states ϕ_j of \check{H} are defined by

$$\check{H} \phi_j = \epsilon_j \phi_j$$

and ϕ_j and ϵ_j are given by

$$\epsilon_j - E_i = \sum_f \frac{H'_{if} H'^*_{if}}{(\epsilon_j - E_f)} \quad (9)$$

$$\phi_j = c_{ij} \psi_i + \sum_f c_{fj} \psi_f, \text{ where}$$

$$|c_{ij}|^2 = 1 / (1 + \sum_f \frac{H'_{if} H'^*_{if}}{(\epsilon_j - E_f)^2}) \quad (10)$$

$$\text{and } c_{fj} = c_{ij} H'_{if} / (\epsilon_j - E_f)$$

In the model of Bixon and Jortner, the states ψ_f have energies given by $E_f = a + ke$ ($a < e$), and all matrix elements are equal. In this case $H'_{if} = v$, for all states ψ_f , and

$$\epsilon_j - E_i = \frac{\pi v^2}{e} \cot \frac{\pi}{e} (\epsilon_j - E_i - a) \quad (11)$$

$$\begin{aligned} |c_{ij}|^2 &= 1 / \left[1 + \frac{\pi v^2}{e^2} \sec^2 \frac{\pi}{e} (\epsilon_j - E_i - a) \right] \\ &= v^2 / \left[(\epsilon_j - E_i)^2 + v^2 + \left(\frac{\pi v^2}{e} \right)^2 \right] \end{aligned} \quad (12)$$

This gives the expression

$$\Delta E = \sqrt{v^2 + (\pi v^2/e)^2}$$

for the half linewidth of ψ_i in absorption, as $|c_{ij}|^2$ measures the probability of finding the system in the energy eigenvalue ϵ_j when the state ψ_i is produced by light absorption.

A radiative perturbation term in the Hamiltonian is included for a consideration of the absorption process. This has the form

$$\begin{aligned}\check{H}_R(t) &= \check{P} \check{E}(t) \quad \text{for } 0 \leq t \leq t_1 \\ &= 0 \quad \text{otherwise}\end{aligned}$$

The matrix elements of \check{P} are effectively zero for many of the Born-Oppenheimer states. The magnitude of the \check{P} matrix elements depends on the Franck-Condon factors, and on the symmetries of the electronic part of the wavefunctions. When only one Born-Oppenheimer state in an energy region has a non-zero \check{P} matrix element with the ground state, this is the state which is produced by photon absorption. The stationary states of the molecular system, on the other hand, do not have good quantum numbers to describe their electronic and vibrational structure when the Born-Oppenheimer approximation breaks down, and so most states in an energy region have non-zero \check{P} matrix elements. The influence of the radiative perturbation on the system may be most clearly displayed by expressing the amplitude of ψ_i in $\phi(t)$, the state of the system at time t , which is given in the case $v \gg e$, $t - t' \ll \hbar/e$, by

$$\begin{aligned}\langle \psi_i | \phi(t) \rangle &= -\frac{1}{\hbar} P_{0i} e^{-(t-t_1)/2\tau} e^{-iE_i t/\hbar} \\ &\cdot \int_0^{t_1} e^{(t'-t_1)/2\tau} e^{iE_i t'/\hbar} \check{E}(t') dt' \quad (13)\end{aligned}$$

where $\tau = \hbar/2\pi v^2$.

The probability of locating the molecule in ψ_i at time t is

$$|\langle \psi_i | \phi(t) \rangle|^2 = \frac{P_{0i}^2}{\hbar^2} e^{-(t-t_1)/\tau} \int_0^{t_1} \int_0^{t_1} e^{(t'+t''-2t_1)/2\tau} e^{-iE_i(t''-t')/\hbar} E(t') E(t'') dt' dt''$$

A consideration of the conventional light source leads to

$$\langle E(t') E(t'') \rangle = 8\pi I_0 \delta(t'-t'') / c, \text{ and so}$$

$$|\langle \psi_i | \phi(t) \rangle|^2 = \frac{8\pi^2 P_{0i}^2 I_0}{\hbar^2 c} e^{-(t-t_1)/\tau} \tau (1 - e^{-t_1/\tau}) \quad (14)$$

This equation displays an exponential decay of the state ψ_i following an irradiation time t_1 . The rate constant for this decay is given by $2\pi v^2/\hbar e$, which is identical with the Fermi Golden Rule expression⁸¹. Bixon and Jortner's treatment is thus very successful in explaining the mechanism for intramolecular relaxation, and the observed rates are explained qualitatively. There are other features, however, which cannot be described by their model. The most important of these questions is the value to be used for v , the constant matrix element which couples the initial state with each of the final states. Values of the actual matrix elements typically range over twenty orders of magnitude, even in a narrow energy neighbourhood. Whether the rate is governed by the largest of them, or by an arithmetic or a geometric mean, or by some more complex mean is not completely clear from Bixon and Jortner's treatment.

If the expressions for the general case are used without recourse to Bixon and Jortner's simple model, however, the mathematical expressions lose their ready solubility, and little progress can be made. The expressions for the probability of finding the system in a state ψ_i or ψ_f after time t can be found if it is assumed that the system is in the state ψ_i at $t=0$, rather than using the more correct approach of allowing interaction with the radiation field.

$$|\langle \psi_i | \phi(t) \rangle|^2 = \sum_j |c_{ij}|^4 + \sum_j \sum_{k < j} 2|c_{ij}|^2 |c_{ik}|^2 \cos(\epsilon_j - \epsilon_k)t/\hbar \quad (15)$$

$$|\langle \psi_f | \phi(t) \rangle|^2 = \sum_j |c_{ij}|^2 |c_{fj}|^2 + \sum_j \sum_{k < j} 2|c_{ij}| |c_{ik}| |c_{fj}| |c_{fk}| \cos(\epsilon_j - \epsilon_k)t/\hbar \quad (16)$$

The expectation values of these quantities at large t are seen to be $\sum_j |c_{ij}|^4$ and $\sum_j |c_{ij}|^4 |H_{if}|^2 / (\epsilon_j - E_f)^2$, respectively. It is apparent that the former quantity will be very small if there are a large number of states ϕ_j , and a fairly even distribution of $|c_{ij}|^2$ among them (since $\sum_j |c_{ij}|^2 = 1$). The dependence of the latter quantity on the magnitude of H_{if} is not so easy to demonstrate. It is possible to show, however, that the expectation value of a particular state ψ_f at large t is roughly proportional to

$$1/[1 + (E_f - E_i)^2/4|H_{if}|^2]^2$$

Thus, in the region where $H_{if} \gg |E_f - E_i|$, the expected population of all states ψ_f after a long time is fairly

similar, regardless of the size of H_{if} . Where $H_{if} < |E_f - E_i|$, the expected population is smaller, and decreases quartically with decreasing H_{if} or increasing $|E_f - E_i|$. The effect of this result is to introduce a weighting in favour of final states ψ_f which have large H_{if} . The weighting is relatively slight, however, and in molecular systems with dense ψ_f , the weighting in favour of the states with high H_{if} , such as those appearing in spectral progressions, is not sufficient to overcome the fact that these states form only a very small proportion of the total states. The emission from the states ψ_f observed in the dilute gas fluorescence of naphthalene, anthracene, and tetracene, is predominantly from the zero quantum level of the modes which appear in progressions simply because the number of these states is much larger than the number of states with higher quantum vibrations in these modes. The fact that the latter states have higher matrix elements, and therefore slightly larger expected populations is not sufficient to overcome their numerical deficiency.

On the evidence, then, it appears that the mechanism of radiationless transitions is fairly well understood in a qualitative sense. The factor which is rate determining for radiationless transitions of large molecules in the dilute gas phase is an intramolecular relaxation of a non-stationary state produced by photon absorption. Electronic excitation energy is transformed to molecular vibrational energy as the initial state decays into states of essentially the same

total energy. The large number of the latter states ensures that this process goes effectively to completion. In condensed phases, vibrational energy may be rapidly dissipated by interactions with the surrounding medium, as it can in the gas phase if the collision time is short. Direct dissipation of the energy from the initially produced state, as proposed in Gouterman's theory, does not appear to be capable of explaining the observed facts. Finally, the rate constant for the intramolecular relaxation process obtained from Bixon and Jortner's treatment of a model containing discrete states is exactly analogous to that arising from Fermi's golden rule, which suggests that a quasi-continuum treatment of the dense manifold of discrete states will probably be valid.

CHAPTER 5: A SIMPLE MODEL FOR RADIATIONLESS TRANSITIONS

(i) The Nature of the Problem

The problem of intramolecular non-radiative transitions between the various bound electronic states of large molecules seems to have been solved in the treatments reviewed in the last chapter, insofar as a qualitative explanation of these processes, and some of the phenomena associated with them, has been shown to arise naturally out of a quantum mechanical treatment of simple models of the experimental situation. There is still much to be desired in the treatment of the phenomena, however. Very few correlations between experimental measurements and results of the theory can be made; those that are made are restricted to crude order of magnitude approximations to rates, or to qualitative or parametric discussions of isotope effects. No useful predictions of the spectral properties of large molecules can be made (beyond the spectroscopist's usual rules of thumb). No critical test of the theory in its present form has been suggested.

There are several good reasons for this situation. The first is the fact that not many measurements are available. The rates are usually the only quantities related to radiationless transitions that can be experimentally obtained. Even these quantities can be measured only by indirect means, in certain molecules which behave favourably. The rate of an

internal conversion is measured only by its competition with a radiative process: lifetimes of fluorescent species, and quantum yields of fluorescence can be measured; the deficiency in the quantum yield must be made up by radiationless processes. When no fluorescence is observed, only an upper bound to the lifetime of the excited state can be deduced. An order of magnitude estimate for processes in the 10^{-12} second region is obtained from the apparent uncertainty broadening of the absorption lines. Intersystem crossing into the metastable first triplet state can be measured directly by triplet-triplet absorption spectroscopy⁸², or, if a steady state is set up, by electron spin resonance spectroscopy. The bulk of the information about radiationless processes which could be available would concern differences in rates of various processes between isotopically substituted species⁶⁹. The other reason for the situation is that any treatment more sophisticated than the very simple models used by Bixon and Jortner, would require some knowledge of a large number of molecular parameters to describe the molecule under consideration. These quantities themselves are known in only a very few cases, and are unlikely to be measurable in many more cases. The third reason lies again in the complexity of the large molecular system: the difficulty will become apparent in the later sections of this thesis. The quasi-continuum of vibrational states of a large molecule is a much more complex manifold

than the continua which are usually treated in related problems. In particular, the matrix elements for various states in the manifold do not form a simple function of energy, but vary over many orders of magnitude, even in a narrow energy neighbourhood. The results of a quantitative treatment may be extremely sensitive to unmeasurably small parameter changes, and the coincidental placing of individual states in the energy spectrum may have important effects.

The work of Siebrand^{68,69} and Siebrand and Williams^{67,70} is an attempt to consider more explicitly the properties of a particular molecule in a treatment of its radiationless transitions. The treatment outlined in this chapter has a similar aim.

(ii) Time Development of a Non-Stationary State

The radiationless decay of electronically excited states of large molecules is due to the fact that photon absorption does not lead to a stationary state of a large molecular system. This arises naturally from a quantum mechanical treatment, where there is a term in the correct total Hamiltonian coupling the molecular states with the radiation field states. The interaction which leads to photon absorption produces an excited state of the molecule from the ground state. This state may be expressed in a basis of molecular stationary states, in which case its amplitudes are time independent. The initial phases of the different

states have an important interrelation, however, and the probability and the frequency of photon emission from the excited state is critically dependent on the relative phases, as well as the amplitudes of the stationary states at the time of emission. A much simpler picture is obtained if a Born-Oppenheimer set of states is used as a basis. In most cases the photon absorption process leads essentially to a single Born-Oppenheimer state. This is a result of the Franck-Condon principle, which arises from the fact that no large change can take place in the nuclear coordinates or the nuclear momentum coordinates during the short time required for photon absorption. In general there is only one state in an energy neighbourhood with an appreciable vibrational overlap with the ground state. (This is particularly the case when the energy of the photon absorbed corresponds to excitation into a level of an electronic state carrying little excess vibrational energy.) A similar argument does not apply to the molecular stationary states, where electronic and nuclear wavefunctions are coupled, and a set of approximate nuclear positions and momenta from the ground state could occur in any of a large number of stationary states in an energy neighbourhood.

An integrated treatment of the experimental situation in which isolated molecule radiationless transitions are observed would consider the entire absorption-decay process in terms of two perturbations. The first arises from coupling

between the molecule and the radiation field, while the second is an artificial intramolecular perturbation, which is present solely because of the choice of a basis set of functions which are eigenfunctions of an approximate, rather than an exact Hamiltonian. The absorption process is treated as the interaction between the system and a photon flux, which is then "switched off". The time development of the system thereafter is a twofold process: on the one hand there is the intramolecular time development of the non-stationary state initially produced, while concurrently, there is a time development due to interaction between the molecular system and the vacuum radiation field, resulting in relaxation accompanied by photon emission. The measurable quantities which would arise from this treatment are the overall lifetime of the excited state and the probability of photon emission.

A simpler approach is to avoid explicit consideration of the radiation field. The system is assumed prepared at $t = 0$ in a non-stationary state of the molecular Hamiltonian (the Born-Oppenheimer state produced by photon absorption). The time development of this state is considered and its rate of decay is obtained. This rate for the radiationless process is given from the observables, the overall lifetime τ_{overall} , and the quantum yield of fluorescence, ϕ_F , by

$$\tau_{\text{radiationless}} = \tau_{\text{overall}} / (1 - \phi_F) \quad (1)$$

This equation shows the radiationless and radiative decay processes as competing, non-interacting mechanisms which can be described by first order kinetics. The condition that the mechanisms do not interact is that the perturbation matrix elements between the final states accessible to each process should be zero. This condition is fulfilled in nearly all practical cases. The radiative process leads to a low molecular energy state, where the radiationless process conserves molecular energy, while transforming some of the electronic energy to vibrational energy. The states resulting from the two processes from an initial excited state are thus not coupled by an interaction matrix element from the radiationless perturbation (as they contain different numbers of photons), nor are they appreciably coupled by the radiative perturbation, as a radiationless process followed by a photon emission would tend to result in retention of a larger amount of molecular vibrational energy and a longer wavelength photon than in the state produced by direct photon emission.

The time development of a non-stationary state may be conveniently treated in several ways. The approaches discussed here are the use of first order time-dependent perturbation theory, and the damping theory developed by Heitler and Ma⁸³. The former treatment displays clearly the approximations and the correction terms arising from the first order treatment of time dependence. In the latter

treatment these are all introduced in the single assumption that the damping function, Γ , varies slowly with energy. The damping theory approach does, however, give a simpler description of the correction terms due to higher orders of configuration interaction.

The first order time-dependent treatment of a stationary perturbation is a well-known approach, which is discussed in most elementary Quantum Mechanics textbooks. A series of states ϕ_j which are eigenfunctions of an approximate Hamiltonian \check{H}^0 is considered. The modulated states $\bar{\phi}_j(t)$ are then solutions of the time-dependent Schrodinger equation under \check{H}^0 .

$$\bar{\phi}_j(t) = \phi_j e^{-i\epsilon_j t/\hbar} \quad (2)$$

$$\check{H}^0 \bar{\phi}_j(t) = i\hbar \frac{\partial}{\partial t} \bar{\phi}_j(t) \quad (3)$$

The effect of a perturbation \check{h} on one of the states $\bar{\phi}_i$ is given by the wavefunction $\Psi(t)$, defined by

$$(\check{H}^0 + \check{h}) \Psi(t) = i\hbar \frac{\partial}{\partial t} \Psi(t) \quad (4)$$

with the boundary condition $\Psi(0) = \phi_i$

The function Ψ may be expanded in terms of $\bar{\phi}$ at any instant of time

$$\Psi(t) = \sum_j a_j(t) \bar{\phi}_j(t) \quad (5)$$

If the expansion in (5) is substituted in (4) several terms in the expression cancel due to equation (3), and the result is

$$\sum_j a_j(t) \check{h} \bar{\phi}_j(t) = \sum_j i\hbar \bar{\phi}_j(t) \frac{\partial}{\partial t} a_j(t) \quad (6)$$

The expression (6) is multiplied on both sides by $\bar{\phi}_k^*(t)$, and integrated over space. When the expressions given in (2) are substituted for $\bar{\phi}$, the result is

$$\sum_j a_j(t) e^{-i(\epsilon_j - \epsilon_k)t/\hbar} \int \phi_k^* \check{h} \phi_j d\tau = i \hbar \frac{\partial}{\partial t} a_k(t) \quad (7)$$

The integral $\int \phi_k^* \check{h} \phi_j d\tau$ will be written in the usual matrix notation as h_{kj} . For the system under consideration \check{H}^0 is the Born-Oppenheimer Hamiltonian, ϕ_i is a vibrational level of an excited electronic state, while all of the other ϕ_j are the various vibrational levels of a lower electronic manifold. The following assumptions are therefore made about \check{h} :

$$h_{jj} = 0 \text{ for all } j; h_{jk} = 0 \text{ for all } k \neq j \neq i;$$

$$h_{ij} = h_{ji}^* \text{ are the only non-zero matrix elements.}$$

In this case equation (7) simplifies to

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} a_i(t) &= \sum_{j \neq i} a_j(t) e^{-i(\epsilon_j - \epsilon_i)t/\hbar} h_{ij} \\ i\hbar \frac{\partial}{\partial t} a_j(t) &= a_i(t) e^{-i(\epsilon_i - \epsilon_j)t/\hbar} h_{ij}^* \quad (j \neq i) \end{aligned} \quad (8)$$

If $a_i(t)$ is expanded in a Taylor series

$$a_i(t) = \sum_{n=0}^{\infty} \frac{t^n}{n!} \left[\frac{\partial^n}{\partial t^n} a_i(t) \right]_0$$

it can be seen that the approximation $a_i(t) \approx 1$ is the zero order result. If this is substituted in the second relation in (8), the resulting expression for $a_j(t)$ is

$$a_j(t) \simeq \frac{h_{ij}^*}{\epsilon_i - \epsilon_j} (e^{-i(\epsilon_i - \epsilon_j)t/\hbar} - 1) \quad (9)$$

The probability amplitude of $\bar{\Phi}_j$ in Ψ is given by

$$a_j^*(t) a_j(t) = \frac{h_{ij}^* h_{ij}}{(\epsilon_i - \epsilon_j)^2} [2 - 2 \cos(\epsilon_i - \epsilon_j)t/\hbar] \quad (10)$$

The probability amplitude of Φ_i is therefore

$$1 - \sum_{j \neq i} a_j^*(t) a_j(t) = 1 - \sum_{j \neq i} \frac{h_{ij}^* h_{ij}}{(\epsilon_i - \epsilon_j)^2} [2 - 2 \cos(\epsilon_i - \epsilon_j)t/\hbar] \quad (11)$$

The expression in (11) can be replaced by the integral form

$$|\langle \bar{\Phi}_i(t) | \Psi(t) \rangle|^2 = 1 - \int_{-\infty}^{\infty} 2(1 - \cos \epsilon t/\hbar) / \epsilon^2 \cdot \sum_{j \neq i} h_{ij}^* h_{ij} \delta(\epsilon_i - \epsilon_j - \epsilon) d\epsilon \quad (11a)$$

which can be approximately integrated to give

$$|\langle \bar{\Phi}_i(t) | \Psi(t) \rangle|^2 = 1 - \frac{2\pi t}{\hbar} \frac{d}{d\epsilon} \left(\sum_{j \neq i}^{\epsilon_j \leq \epsilon} h_{ij}^* h_{ij} \right)_{\epsilon = \epsilon_i} \quad (12)$$

In this equation, which is valid only for small t , the first order rate constant for decay of the state $\bar{\Phi}_i$ under the influence of the perturbation \tilde{h} is given by

$$\text{Rate} = \frac{2\pi}{\hbar} \frac{d}{d\epsilon} \left(\sum_{j \neq i}^{\epsilon_j \leq \epsilon} h_{ij}^* h_{ij} \right)_{\epsilon = \epsilon_i} \quad (13)$$

If the integral in (11a) is evaluated completely, the correction term will be an integral involving the derivative of a delta function. However, in practice, this will just be a highly peaked dipolar function, just as the sum in (12)

will not be a step function, but a function with rounded corners, which will, in the case of closely spaced ϵ_j , become a smooth function. The reason for this is the slight lack of definition of ϵ_j due to the linewidth of the states being considered. With this understanding it becomes clear that the correction term is probably small because of the tendency to cancellation between the two lobes of the dipolar function. In any case its probable effect is just to cause a further smoothing of the Rate versus Energy function.

The alternative approach is to use the damping theory formalism developed by Heitler and Ma⁸³. The system is again considered in the basis of zero order states, Φ_j . The equation (7) is used to describe the amplitudes of the various basis functions. In order to obtain an expression which is valid for negative as well as positive time, the boundary conditions are altered, and an inhomogeneous term appears in (7)

$$i \hbar \frac{\partial}{\partial t} a_j(t) = \sum_k h_{jk} a_k(t) e^{-i(\epsilon_k - \epsilon_j)t/\hbar} + i \hbar \delta_{ij} S(t) \quad (7a)$$

This is used with the boundary condition $a_j(t) = 0$ for all $t < 0$, and the inhomogeneous term ensures that $a_i(+0) = 1$ (i.e. $a_i(t) \rightarrow 0$ as $t \rightarrow 0$ from above). A Fourier transformation of a_k and S leads to the equation

$$(E - \epsilon_j) g_j(E) = \sum_k h_{jk} g_k(E) + S_{ij} \quad (14)$$

Division by $(E - \epsilon_j)$ to obtain values of g is arbitrary when $E = \epsilon_j$. The division chosen to satisfy (7a) is in

$$\zeta(E - \epsilon_j) = \mathcal{P} \left(\frac{1}{E - \epsilon_j} \right) - i\pi \delta(E - \epsilon_j),$$

where $\mathcal{P} \left(\frac{1}{E - \epsilon_j} \right)$ is related to the Cauchy Principal Value of an integral, and takes the values $\frac{1}{E - \epsilon_j}$ for $E \neq \epsilon_j$, and 0 for $E = \epsilon_j$

From (14) these relations are obtained:

$$u_k(E) = h_{ik}^* + \sum_{j \neq i} u_j(E) h_{kj} \zeta(E - \epsilon_j) \quad (15)$$

where $u_k(E) = g_k(E) / g_i(E)$, and also

$$g_i(E) = 1 / [E - \epsilon_i + \frac{1}{2} \mathcal{H} \Gamma_i(E)] \quad (16)$$

$$\text{where } \frac{1}{2} \mathcal{H} \Gamma_i(E) = i h_{ii} + i \sum_{j \neq i} h_{ij} u_j(E) \zeta(E - \epsilon_j)$$

The amplitudes of the state $\Psi(t)$, $a_j(t)$, are then obtained by inverting the expressions for $g_j(E)$.

$$a_i(t) = -\frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{e^{i(\epsilon_i - E)t/\mathcal{H}}}{E - \epsilon_i + \frac{1}{2} \mathcal{H} \Gamma_i(E)} dE \quad (17)$$

$$a_j(t) = -\frac{1}{2\pi i} \int_{-\infty}^{\infty} u_j(E) \zeta(\epsilon_j - E) \frac{e^{i(\epsilon_j - E)t/\mathcal{H}}}{E - \epsilon_j + \frac{1}{2} \mathcal{H} \Gamma_i(E)} dE \quad (18)$$

If it is assumed that $\Gamma_i(E) = \Gamma$, then the integral in (17) gives $a_i(t) = e^{-\frac{1}{2}\Gamma t}$, and so the probability amplitude of state Φ_i in $\Psi(t)$ is

$$a_i^*(t) a_i(t) = e^{-\mathcal{R}(\Gamma)t} \quad (17a)$$

where $\mathcal{R}(\Gamma)$ is the real part of the quantity Γ . The state Φ_i therefore undergoes an exponential decay, with a rate constant given by $\mathcal{R}(\Gamma)$. The real part of the function $\Gamma_i(E)$ is given by

$$-\frac{2}{\mathcal{H}} \mathcal{P} \left[\sum_{j \neq i} h_{ij} u_j(E) \zeta(E - \epsilon_j) \right] \quad (19)$$

Successive approximations to $u_j(E)$ can be obtained from (15).

In the first approximation, $u_j(E) = h_{ij}^*$, and the rate is given by

$$\text{Rate}^{(1)} = \frac{2\pi}{N} \sum_{j \neq i} h_{ij}^* h_{ij} \delta(E - \epsilon_j) \quad (20)$$

The second approximation gives $u_j(E) = h_{ij}^* + \sum_{k \neq i} h_{ik}^* h_{kj}^* \delta(E - \epsilon_k)$

The rate in this case becomes

$$\text{Rate}^{(2)} = \text{Rate}^{(1)} + \sum_{j \neq i} \sum_{k \neq i} \frac{2\pi}{N} \left[h_{ij} h_{ik}^* h_{kj}^* + h_{ij}^* h_{ik} h_{kj} \right] \frac{\delta(E - \epsilon_j)}{E - \epsilon_k} \quad (21)$$

The third order approximation becomes much more complicated.

$$\begin{aligned} \text{Rate}^{(3)} = \text{Rate}^{(2)} + \sum_{j \neq i} \sum_{k \neq i} \sum_{l \neq i} \frac{\pi}{N} \frac{\delta(E - \epsilon_j)}{(E - \epsilon_k)(E - \epsilon_l)} & \left[h_{ij} h_{ik}^* \right. \\ & h_{kl} h_{lj} + h_{ij} h_{il}^* h_{kl} h_{jk} + h_{ik} h_{il}^* h_{lj} h_{jk} + h_{ij}^* h_{ik} h_{kl} h_{lj} + \\ & \left. h_{ij}^* h_{il} h_{kl} h_{jk} + h_{ik}^* h_{il} h_{lj} h_{jk} \right] \end{aligned} \quad (22)$$

By a suitable permutation of indices, it can be shown that the two terms containing no h_{ij} reduce to the form

$$\frac{2\pi}{N} \sum_k \sum_l \frac{h_{ik} h_{kj} h_{il}^* h_{lj}^*}{(\epsilon_j - \epsilon_k)(\epsilon_j - \epsilon_l)} \delta(E - \epsilon_j)$$

These terms may be included with the $\text{Rate}^{(2)}$ expression to give

$$\text{Rate}^{(2')} = \frac{2\pi}{N} \sum_j \left| h_{ij} + \sum_k \frac{h_{ik} h_{kj}}{E - \epsilon_k} \right|^2 \delta(E - \epsilon_j) \quad (23)$$

The other terms may be reduced in a similar manner to

$$\text{Rate}^{(3)} = \text{Rate}^{(2')} + \frac{\pi}{H} \sum_j \sum_k \sum_l \delta(E - \epsilon_j)$$

$$\left[\frac{h_{ij} h_{il}^* h_{lk}^* h_{kj}^* + h_{ij}^* h_{il} h_{lk} h_{kj}}{(E - \epsilon_l)(E - \epsilon_k)} \right]$$

which rearranges, with an interchange of k and l indices, to

$$\begin{aligned} \text{Rate}^{(3)} = \text{Rate}^{(2')} + \frac{2\pi}{H} \sum_j \delta(E - \epsilon_j) \\ \cdot \sum_k \sum_l \frac{h_{ij}^* h_{il}^* h_{lk}^* h_{kj}^* + h_{ij}^* h_{il} h_{lk} h_{kj}}{(E - \epsilon_l)(\epsilon_l - \epsilon_k)} \end{aligned} \quad (24)$$

It is thus apparent that

$$\begin{aligned} \text{Rate}^{(3')} = \frac{2\pi}{H} \sum_j \left[h_{ij} + \sum_k \frac{h_{ik} h_{kj}}{E - \epsilon_k} + \sum_k \sum_l \frac{h_{il} h_{lk} h_{kj}}{(E - \epsilon_l)(\epsilon_l - \epsilon_k)} \right] \delta(E - \epsilon_j) \end{aligned} \quad (25)$$

The various functions for Rate do not describe the actual rate of an exponential decay, as equation (17a) is derived assuming that $\Gamma_i(E)$ is independent of E . An interpretation of the real part of $\Gamma_i(E)$ as a sum of delta functions is thus internally inconsistent as a rate equation, as such a sum exhibits the strongest possible dependence on the exact value of E . The expression is valid if the states ϕ_j are relatively dense in the energy region, and the Dirac delta functions are interpreted as finite functions, highly peaked about ϵ_j , which sum to produce a smooth curve for Rate versus the parameter E .

In this section the expressions which will be used to describe the rates of radiationless transitions as a function of the energy of the various states have been

derived in equations (13) and (20), which are equivalent. The treatments have been extended to gain some insight into the correction terms arising from some of the approximations made. Difficulties which arise in treating manifolds of discrete states rather than true continua were evident in several steps, so that the resulting rate expressions appear in the formalism containing Dirac delta functions. These are to be interpreted as finite peaked functions which sum, when the states are sufficiently dense, to produce smooth rate versus energy functions. A similar difficulty which would have arisen in Bixon and Jortner's treatment was bypassed in the approximation of a sum with an integral (Reference 75, Equations (37) to (40)).

(iii) The Harmonic Approximation

When the electronic wavefunction in the Born expansion is restricted to a function of electronic coordinates only, the effective potential which governs the nuclear motions is a quadratic function of the nuclear coordinates. In this case it is possible to achieve a great simplification of the nuclear problem by choosing a transformed set of nuclear coordinates which reduce the vibrational wavefunction to a product of linear harmonic oscillator wavefunctions in these coordinates. The equation for the vibrational motions in a molecule in the Born-Oppenheimer approximation is

$$\sum_Y \frac{\hbar^2}{2m_Y} \nabla_Y^2 \chi(\underline{r}_X, \underline{r}_Y, \dots) + V(\underline{r}_X, \underline{r}_Y, \dots) \chi(\underline{r}_X, \underline{r}_Y, \dots) = E \chi(\underline{r}_X, \underline{r}_Y, \dots) \quad (26)$$

The origin of the nuclear coordinates may be placed at the equilibrium position, i.e. that which minimizes the effective potential, and this potential may be chosen as an arbitrary zero on the energy scale. In this case, the most general harmonic potential may be written

$$V(x_i, \dots) = \sum_j \sum_k f_{jk} x_j x_k \quad (27)$$

where x_i may be any of x_Y , y_Y , or z_Y . m_i refers to m_Y for x_Y , y_Y , or z_Y . The normal coordinates are first rescaled to take account of the mass.

$$x'_k = x_k \sqrt{m_k}$$

This leads to the equation

$$-\frac{\hbar^2}{2} \sum_k \frac{\partial^2}{\partial x'^2_k} \chi + \sum_j \sum_k \frac{f_{jk}}{\sqrt{m_j m_k}} x'_j x'_k \chi = E \chi \quad (28)$$

New coordinates q_n are measured in directions \underline{u}_n which are defined by a unitary transformation of the unit vectors of x'_i , given by the eigenvalue equation

$$\sum_k \frac{f_{jk}}{\sqrt{m_j m_k}} u_{nk} = \lambda_n u_{nj} \quad (29)$$

Equation (26) then becomes

$$-\frac{\hbar^2}{2} \sum_j^{N+6} \frac{\partial^2}{\partial q_j^2} \chi + \lambda_j q_j^2 \chi = E \chi \quad (30)$$

χ may be expressed as $\prod_j^{N+6} \chi_j(q_j)$, where $\chi_j(q_j)$ is given by

$$-\frac{\mu^2}{2} \frac{\partial^2}{\partial q_j^2} \chi_j(q_j) + \lambda_j q_j^2 \chi_j(q_j) = \epsilon_j \chi_j(q_j) \quad (31)$$

In a large molecule, six values of λ_j will be zero. These will be for nuclear coordinates which correspond to translations or rotations of the whole molecule, and may simply be deleted from the wavefunction when these motions are not being explicitly considered. The other λ_j will all be positive, and the functions $\chi_j(q_j)$ are given by⁸⁴:

$$\epsilon_{jn} = (n + \frac{1}{2}) \mu \omega_j$$

$$\chi_{jn}(q_j) = \left(\frac{\omega_j}{\pi \mu} \right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} e^{-\omega_j q_j^2 / 2\mu} H_n(q_j \sqrt{\omega_j / \mu}) \quad (32)$$

Note that as defined q_j has dimensions (length) \times (mass)^{1/2}. H_n is the n th. Hermite polynomial, and is given by

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}$$

ω_j is equal to $\sqrt{2\lambda_j}$. In the vibrational problem, the coordinates q_j of a point, and the characteristic frequencies, ω_j are different for different electronic states of a molecule. In most cases, the directions of the normal coordinates, u_k , remain unaltered to a good approximation. The equilibrium geometry of the molecule does differ for different electronic states, and this results in an origin shift of the nuclear normal coordinates. Similarly the force constants which govern the potential function, and hence the values of ω_j , differ for different states. The matrix

elements for the breakdown of the Born-Oppenheimer approximation, which govern the rates of the radiationless processes in the model discussed, involve overlap integrals between the various eigenfunctions of the vibrational problems for the initial and final states. The evaluation of overlap integrals for harmonic oscillator wavefunctions has been attempted by Hutchisson⁸⁴ and Manneback⁸⁵. Recurrence relations⁸⁵, and published tables⁸⁶ are available for these functions. A more extensive table was compiled during the course of this project. The recurrence relations obtained by Manneback are

$$\begin{aligned}
 \langle \chi'_1 | \chi''_k \rangle &= \rho \sqrt{\frac{k-1}{k}} \langle \chi'_1 | \chi''_{k-2} \rangle + \sqrt{1-\rho^2} \sqrt{\frac{1}{k}} \langle \chi'_{1-1} | \chi''_{k-1} \rangle \\
 &\quad + M \sqrt{1-\rho} \sqrt{\frac{1}{k}} \langle \chi'_1 | \chi''_{k-1} \rangle \\
 &= -\rho \sqrt{\frac{1-1}{-1}} \langle \chi'_{1-2} | \chi''_k \rangle + \sqrt{1-\rho^2} \sqrt{\frac{k}{1}} \langle \chi'_{1-1} | \chi''_{k-1} \rangle \\
 &\quad - M \sqrt{1+\rho} \sqrt{\frac{1}{1}} \langle \chi'_{1-1} | \chi''_k \rangle
 \end{aligned} \tag{33}$$

where the parameters are defined by

$$M = (q' - q'') \sqrt{\omega' \omega'' / k(\omega' + \omega'')}$$

$$\rho = (\omega'' - \omega') / (\omega'' + \omega')$$

The value of $\langle \chi'_0 | \chi''_0 \rangle$ is given by

$$\langle \chi'_0 | \chi''_0 \rangle = (1-\rho^2)^{\frac{1}{4}} e^{-\frac{1}{2}M^2} \tag{33a}$$

The overall vibrational overlap function is given by a product over all of the modes.

$$\langle \chi'(l_1 \dots) | \chi''(k_1 \dots) \rangle = \frac{N}{n_j} \langle \chi'_{jl}(q_j^I) | \chi''_{jk}(q_j^II) \rangle \quad (34)$$

Finally, the Born-Oppenheimer breakdown requires the evaluation of matrix elements of the type

$$\langle \chi'(l_1 \dots) | \text{grad}_q | \chi''(k_1 \dots) \rangle$$

By differentiating equation (32), and considering the properties of the Hermite polynomials, one obtains the following relation.

$$\begin{aligned} \frac{\partial}{\partial q_j} |\chi_{jl}(q_j)\rangle &= |\chi_{j(l+1)}(q_j)\rangle \cdot \sqrt{\frac{n+1}{2}} \sqrt{\frac{\omega}{M}} - |\chi_{j(l-1)}(q_j)\rangle \\ &\quad \cdot \sqrt{\frac{n}{2}} \sqrt{\frac{\omega}{M}} \end{aligned} \quad (35)$$

With the use of this result, all matrix elements involving vibrational functions can be reduced to the vibrational overlap functions given by (33) and (33a).

(iv) Evaluation of the Rate Function

In an earlier section the time development of a non-stationary state was considered in the case where the state forms part of a basis of orthogonal states which are discrete, and fairly dense in the energy region. When the basis is chosen so that the only coupling occurs between the initial state and each of the other states, a rate function for the decay of the state can be obtained in the form of equation (13). Equation (13) is amenable to the treatment outlined in section (iii) of chapter 1. The expression

$$\text{Rate} = \frac{2\pi}{M} \frac{d}{dt} \left(\sum_{\substack{f \\ \epsilon_f \leq \epsilon}} h_{if}^* h_{if} \right) \epsilon = \epsilon_i \quad (13)$$

may be replaced by

$$\text{Rate} = \frac{2\pi}{\hbar} \frac{d}{d\varepsilon} \left\{ \int_{-\infty}^{\varepsilon} \sum_f h_{if}^* h_{if} \delta(\varepsilon_f - \varepsilon) d\varepsilon \right\}_{\varepsilon=\varepsilon_i}, \text{ which is}$$

identical with equation (20). The Laplace transform of the Rate, if Rate is regarded as a function of ε , rather than simply being evaluated at $\varepsilon = \varepsilon_i$, is given by

$$\mathcal{L}_p(\text{Rate}) = \frac{2\pi}{\hbar} \sum_f h_{if}^* h_{if} e^{-\varepsilon_f p} \quad (36)$$

At this point the form of the matrix elements h_{if} , and the energy eigenvalues, ε_f , is considered in more detail. The initial state ψ_i is a Born-Oppenheimer state involving an excited electronic wavefunction, and a nuclear wavefunction appropriate to the electronic state. The states ψ_f are all vibrational states of a lower energy electronic state. The electronic and nuclear parts of the wavefunctions will be denoted ϕ^I , $\chi^I(i)$, ϕ^F , and $\chi^F(f)$ respectively:

$$\psi_i = \phi^I \chi^I(i) ; \psi_f = \phi^F \chi^F(f)$$

The matrix element h_{if} is given by the equation (7) of chapter 4 as:

$$h_{if} = \hbar^2 \langle \phi^I | \underbrace{\text{grad}_q}_{\text{vector gradient}} | \phi^F \rangle \cdot \langle \chi^I(i) | \underbrace{\text{grad}_q}_{\text{vector gradient}} | \chi^F(f) \rangle \\ + \frac{\hbar^2}{2} \langle \phi^I | \nabla_q^2 | \phi^F \rangle \langle \chi^I(i) | \chi^F(f) \rangle$$

where $\underbrace{\text{grad}_q}_{\text{vector gradient}}$ is a vector gradient function taken with respect to nuclear coordinates which include the nuclear masses.

When the harmonic approximation is used, a separation in terms of the normal coordinates can be performed, and the resulting relation is

$$\begin{aligned}
h_{if} = & \frac{1}{2} \hbar^2 \langle \phi^I | \sum_j^N \frac{\partial^2}{\partial q_j^2} | \phi^F \rangle \prod_k^N \langle \chi_{ki}^I | \chi_{kf}^F \rangle \\
& + \hbar^2 \sum_j \langle \phi^I | \frac{\partial}{\partial q_j} | \phi^F \rangle \prod_{k \neq j}^N \langle \chi_{ki}^I | \chi_{kf}^F \rangle \cdot \langle \chi_{ji}^I | \frac{\partial}{\partial q_j} | \chi_{jf}^F \rangle
\end{aligned}
\tag{37}$$

For convenience, the electronic matrix elements are abbreviated to A and B_j , and the angular frequencies ω_j are replaced with energy variables $\nu_j = \hbar \omega_j$. Then, using (35), equation (37) becomes

$$\begin{aligned}
h_{if} = & \frac{1}{2} \hbar^2 A \prod_k^N \langle \chi_{ki}^I | \chi_{kf}^F \rangle + \hbar \sum_j B_j \sqrt{\nu_j^F} \prod_{k \neq j}^N \langle \chi_{ki}^I | \chi_{kf}^F \rangle \cdot \\
& \left(\sqrt{\frac{n+1}{2}} \langle \chi_{ji}^I | \chi_{j(f+1)}^F \rangle - \sqrt{\frac{n}{2}} \langle \chi_{ji}^I | \chi_{j(f-1)}^F \rangle \right)
\end{aligned}
\tag{38}$$

In the treatment of Siebrand⁶⁸, only the first term of this expression was considered. Bixon and Jortner⁷⁵ suggest that this is not the most important term. It is apparent that the electronic matrix element A will be zero by symmetry unless the states ϕ^I and ϕ^F have the same symmetry representation, as the operator $\sum_j^N \frac{\partial^2}{\partial q_j^2}$ is totally symmetric. Similarly, in molecular systems of high symmetry many of the B_j matrix elements will be zero. The selection rule for non-zero B_j is that the product of the representations of q_j and ϕ^F must contain the representation of ϕ^I .

The value of \mathcal{E}_f is given, from equation (32), by $\sum_j (f_j + \frac{1}{2}) \nu_j^F$. In the treatment of the harmonic approximation the arbitrary zero of the energy scale was taken as the potential minimum in the vibrational problem for the

particular electronic state. It is more convenient in the present treatment to assign energy $\varepsilon_f = 0$ for the zero vibrational state of the electronic state ϕ^F . In this case ε_f for other vibrational states of ϕ^F is given by $\sum_j f_j \nu_j^F$. The energy of the zero vibrational level of the electronic state ϕ^I will be denoted E_0^I . Expressions can be obtained for the various terms in the Laplace transform in equation (36). As a first step these expressions will be evaluated assuming that the state ψ_i is the zero vibrational state of ϕ^I . If $h_{if} = a_{if} + \sum_j b_{jif}$ is used as a convenient abbreviation, then:

$$\frac{2\pi}{N} \sum_f a_{Of}^* a_{Of} e^{-\varepsilon_f p} = \frac{2\pi}{N} A^* A \prod_k^N \left[\sum_f \langle \chi_{k0}^I | \chi_{kf}^F \rangle^2 e^{-f \nu_{kp}^F} \right] \quad (39)$$

The expression in the summation on the right of (39) is clearly a power series in $y_k = \exp(-\nu_{kp}^F)$. The coefficients can be evaluated from the recurrence relations given in equation (33). When this is done, it is found that the power series is the expansion of an expression involving simple functions:

$$\sum_{f_k} \langle \chi_{k0}^I | \chi_{kf}^F \rangle^2 y_k^{f_k} = \sqrt{\frac{1 - \rho_k^2}{1 - \rho_k^2 y_k^2}} e^{-M_k^2 \left(\frac{1 - y_k}{1 - \rho_k y_k} \right)} \quad (40)$$

and so

$$\frac{2\pi}{N} \sum_f a_{Of}^* a_{Of} e^{-\varepsilon_f p} = \frac{2\pi}{N} A^* A \prod_k^N \sqrt{\frac{1 - \rho_k^2}{1 - \rho_k^2 y_k^2}} \cdot e^{-M_k^2 \left(\frac{1 - y_k}{1 - \rho_k y_k} \right)} \quad (41)$$

The expression on the right of equation (40) will be abbreviated with Y_k , as it will occur throughout the other

expressions which are derived. Another term which occurs in the Laplace transform is the diagonal term in b_{j0f} .

$$\begin{aligned} \frac{2\pi}{N} \sum_f b_{j0f}^* b_{j0f} e^{-\epsilon_f p} &= \frac{2\pi}{N} B_j^* B_j \prod_{k \neq j}^N \left[\sum_f \langle \chi_{k0}^I | \chi_{kf}^F \rangle^2 e^{-f \nu_k^F p} \right] \\ &\cdot \sum_f e^{-f \nu_j^F p} \left(\sqrt{\frac{f+1}{2}} \langle \chi_{j0}^I | \chi_{j(f+1)}^F \rangle - \sqrt{\frac{f}{2}} \langle \chi_{j0}^I | \chi_{j(f-1)}^F \rangle \right)^2 \quad (42) \end{aligned}$$

This simplifies to

$$\begin{aligned} \frac{2\pi}{N} \sum_f b_{j0f}^* b_{j0f} e^{-\epsilon_f p} &= \frac{2\pi}{N} B_j^* B_j \prod_k^N Y_k \\ &\cdot \left\{ \frac{y_j^2 (1-\rho_j)^2}{1 - y_j^2 y_j^2} + \frac{M_j^2}{(1 - \rho_j y_j)^2} \left[(1 - y_j)^2 + \rho_j (1 + y_j)^2 - 4 \rho_j^2 y_j^2 \right] \right\} \quad (43) \end{aligned}$$

Similar expressions are obtained for the off-diagonal terms.

$$\frac{2\pi}{N} \sum_f a_{0f}^* b_{j0f} e^{-\epsilon_f p} = \frac{2\pi}{N} A^* B_j \prod_k^N Y_k \cdot M_k \rho_k \frac{1 - y_k}{1 - \rho_k y_k} \sqrt{\frac{1 - \rho_k}{2}} \quad (44)$$

$$\begin{aligned} \frac{2\pi}{N} \sum_f b_{j0f}^* b_{k0f} e^{-\epsilon_f p} &= \frac{2\pi}{N} B_j^* B_k \prod_l^N Y_l \\ &\left[M_j \rho_j \frac{1 - y_j}{1 - \rho_j y_j} \sqrt{\frac{1 - \rho_j}{2}} \right] \cdot \left[M_k \rho_k \frac{1 - y_k}{1 - \rho_k y_k} \sqrt{\frac{1 - \rho_k}{2}} \right] \quad (45) \end{aligned}$$

The Laplace transform in equation (36) is therefore given by

$$\begin{aligned} \mathcal{L}_p (\text{Rate}) &= \frac{2\pi}{N} \left[\prod_l^N Y_l \right] \left[A^* A + \sum_j (B_j^* B_j X_j + A^* B_j Z_j + A B_j^* Z_j) \right. \\ &\quad \left. + \sum_j \sum_k B_j^* B_k Z_j Z_k \right] \quad (46) \end{aligned}$$

A , B_j , and Y_j have already been defined. Z_j and X_j are given

by the following relations.

$$Z_j = M_j \rho_j \frac{1 - y_j}{1 - \rho_j y_j} \sqrt{\frac{1 - \rho_j}{2}} \quad (46a)$$

$$X_j = \frac{y_j^2 (1 - \rho_j)^2}{1 - \rho_j^2 y_j^2} + \frac{M_j^2}{(1 - \rho_j y_j)^2} \left[(1 - y_j)^2 + \rho_j (1 + y_j)^2 - 4 \rho_j^2 y_j^2 \right] \quad (46b)$$

The Laplace transform of the function which describes the rate of radiationless decay as a function of the energy gap between the zero vibrational levels of the two electronic states involved has thus been obtained in a simple, if lengthy form. The parameters on which the result depends are functions of the molecular geometries in the electronic states, the characteristic frequencies of the normal modes in the electronic states, and matrix elements involving the rate of change in electronic wavefunctions along nuclear coordinates. In principle, the former two sets of parameters can be deduced from a spectral analysis. In practice, a complete set of vibrational frequencies is known for the first singlet excited state of benzene, and the more symmetrical deuterobenzenes, but not for any excited state of any larger molecule. However, the modes which will have the largest influence on the rate function will be those with the largest values of ρ and/or M , and many of the frequencies for these modes in larger molecules are known, since they are also the modes which appear most strongly

in spectral progressions, in the vibrational structure of electronic absorption bands.

A means must also be found for estimating A and B_j . Molecular orbital methods suggest themselves here. A large range of choice is available for the compromise which must be reached between accuracy and simplicity, and the practicality of the approach will depend to some extent on the sensitivity of A and B_j values to different methods of approximate evaluation. This problem has not been examined in this work. The electronic matrix elements will be discussed in a later chapter. They will meanwhile be treated as unknown constants.

(v) Inversion of the Laplace Transform

Although a result has been obtained which expresses the Laplace transform of the Rate function as defined in equation (13) in terms of elementary functions of basic molecular properties, this in itself does not provide much useful information about the rates of radiationless transitions predicted by the model used. The inversion of the Laplace transform presents severe difficulties. It is not possible to obtain the inverse Laplace transform in a closed algebraic form. Even if it were, the expression obtained would be a strict sum of delta functions as implied by equation (20). Nowhere in the treatment has any step been made which approximates these functions. The use of the

simple algebraic expressions for ε_k has rather given these quantities a precise definition that they ought not to have because of linewidth. To obtain the inverse Laplace transform an approximate method must be used. No approximate algebraic method has been found for this type of expression: the complexity of the expression, and the fact that in the general case dominant contributions cannot be predicted, appear to rule out such an approach. The method of obtaining the inverse Laplace transform in order to evaluate the Rate function must therefore be an approximate numerical method.

The numerical inversion of a Laplace transform is a difficult computational problem, and no really efficient computer algorithm is available. The methods which are used have been found to be very problem-dependent⁸⁷. The methods fall into two main categories. The first class of methods involves evaluation of the Laplace transform along some complex axis, and reducing the problem to a Fourier transform problem⁸⁸. These problems are much better explored, and many effective but time and core-consuming methods are available. The second class of methods operate by expanding the Laplace transform in terms of functions which are themselves the Laplace transform of a set of orthogonal polynomials. Once the expansion coefficients are obtained, the solution is immediately available^{89,90}.

Both types of method fail on the problem in hand. Methods in the first class have, in some cases, special requirements

for the functions to be well-behaved. Their application to problems involving Dirac delta functions must therefore be carefully examined. The main reason for failure of both types of method is rather different, however. The strict sum of delta functions is a very rapidly varying function with many infinite peaks. The function which is sought is a smooth function which reproduces the general contour of the weighting of the delta function sum. The ideal criterion for a successful approximation $R(\epsilon)$ to $\text{Rate}(\epsilon)$ would be

$$\int_E^{E + \Delta E} \text{Rate}(\epsilon) d\epsilon = \int_E^{E + \Delta E} R(\epsilon) d\epsilon \quad (47)$$

for the largest possible range of E , and the smallest possible ΔE consistent with a smooth curve for the function R . The orthogonal polynomials which are used are generally functions which have a number of nodes equal to the index of the polynomials. The result of this is that the higher order polynomials are more rapidly oscillating functions, and so tend to have larger coefficients in the expansion, as they try to reproduce the delta function sum. The representation diverges, and any selection of an arbitrary limit to the number of terms gives a completely inaccurate function. The method reproduces the wrong feature of the delta function sum: it produces a rapidly varying function, rather than a function which has a similar distribution to the delta function sum. The difficulty is further accentuated by the fact that most methods are weighted to producing a

good approximation $R(\varepsilon)$ to $\text{Rate}(\varepsilon)$ at low values of ε , and this is the region where the delta functions in the sum are sparse, and a smooth function can least adequately reproduce the distribution of $\text{Rate}(\varepsilon)$. A similar difficulty occurs in the Fourier transform part of the computation in the methods in the first class. The computation of an inverse Laplace transform must therefore be re-examined for this particular problem.

The first part of the problem is to decide on the constraints to be placed on the Laplace transform of an approximate function in order that it should conform as well as possible to the criterion expressed in equation (47), particularly when E is large. The most suitable simple constraints appear to be that the value of an approximate Laplace transform at $p=0$ (p being the dummy variable replacing E), and the value of the first k derivatives of the approximate function at $p=0$ should be equated to the corresponding values for the exact function. If the function $L(p)$ is the Laplace transform of $R(\varepsilon)$, and $\mathcal{L}(p)$ is the Laplace transform of $\text{Rate}(\varepsilon)$, then the condition on L

$$L^{(m)}(0) = \mathcal{L}^{(m)}(0)$$

implies the condition on R

$$\int_0^\infty \varepsilon^m R(\varepsilon) d\varepsilon = \int_0^\infty \varepsilon^m \text{Rate}(\varepsilon) d\varepsilon \quad (48)$$

This condition is not as suitable as that required in (47), but it does appear to be a useful constraint. It is biased

in favour of high values of ε , and as higher order terms are taken the bias shifts to higher values of ε . An approximation based on this criterion ought, then, to reproduce the distribution of $\text{Rate}(\varepsilon)$ rather than its property of rapid oscillation, particularly as the condition on $R(\varepsilon)$ is essentially a distribution condition.

The second part of the problem is the type of function to use for the approximate Laplace transform. This is determined either by the observed form of \mathcal{L} or the expected form of R . The function \mathcal{L} defined by (46) is typically a function with a finite value at $p=0$ which descends monotonically with increasing p , asymptotically approaching a fixed positive value, denoted $\mathcal{L}(\infty)$. The form of R is quite uncertain at low ε ; it may oscillate quite irregularly in this region. As ε increases, however, R becomes a smooth, slowly varying function, which rapidly approaches zero as ε increases further. Clearly, a polynomial form is not suitable for R . A form which would be suitable could be a polynomial times a negative exponential. If R has the form

$$R(\varepsilon) = \left(\sum_{k=0}^n a_k \varepsilon^k \right) \cdot e^{-\alpha \varepsilon}$$

then $\mathcal{L}_p(R)$ has the form

$$L(p) = \sum_{k=0}^n \frac{a_k k!}{(p+\alpha)^{k+1}}$$

A form which offers some further advantages is

$$R(\varepsilon) = \sum_{k=0}^n a_k (\varepsilon - \beta)^k e^{-\alpha(\varepsilon - \beta)} \quad \text{when } \varepsilon \geq \beta$$

$$R(\varepsilon) = 0 \quad \text{when } 0$$

The Laplace transform of this function is

$$L(p) = \sum_{k=0}^n \frac{a_k k!}{(p+\alpha)^{k+1}} e^{-\beta p}$$

Values of the parameters a_k , α , and β are assigned by fitting the value of the function $L(p)$ and its first $(n+1)$ derivatives at $p=0$ to the corresponding values of $\mathcal{L}(p)$ as determined numerically from (46). Where alternative sets of solutions are possible, the solution which best fits the value of \mathcal{L} for increasing p is chosen. A constant term, $\mathcal{L}(\infty)$ is subtracted from $\mathcal{L}(p)$ before the fit is made. This simply means that the contribution to the function Rate from the term $\mathcal{L}(\infty) \cdot \delta(\varepsilon)$ is ignored.

The choice of functions for R is a further insurance that the distribution, rather than the rapid oscillation, of Rate will be reproduced by the method. Although the form for an infinite sum of the type shown above will be a complete representation of all possible functions with the general properties of Rate, a rapidly oscillating function can only be produced with large contributions from very high order terms. The distribution can be effectively reproduced from low order terms, so that the representation will converge for a relatively small number of terms, even though it must diverge if a very large number of terms are taken into account.

It appears then, that this is a successful method for numerically obtaining a slowly varying function R which reproduces the distribution of the rapidly varying function Rate. In view of the fact that the criterion (48) is not such a suitable and complete criterion as (47) for the satisfactory reproduction of Rate, it will be necessary to further test the validity of the approximation R as it is obtained for various numerical examples.

(vi) Some Numerical Results

The computation of a function R for a particular pair of electronic states in a molecule, which describes the rate which would be expected for radiationless decay of the zero vibrational level of the higher state into the lower state, as a function of the energy difference between the two states, has been completely outlined in principle. The method is a numerical method, and numerical values are not available for many of the parameters which determine the function. The method does not, therefore, predict actual rates for real molecules. As an indication of the type of function which would be obtained for R , it was assumed that the Laplace transform of Rate had the form

$$\mathcal{L}_p(\text{Rate}) = \text{constant} \cdot \prod_{j=1}^N Y_j$$

This is equivalent to the assumption made in Siebrand's treatment⁶⁸, namely that the rate expressions could be

described in terms of matrix elements which are products of a constant electronic part and a vibrational overlap integral. Equations (46a) and (46b) show that this is not the case.

Values from Table 5-1 were substituted for the characteristic frequencies and geometry changes in benzene and hexadeutero-benzene in the ground ($^1A_{1g}$) and first excited singlet ($^1B_{2u}$) states. A function $L(p)$ approximating $\mathcal{L}(p)$ was then obtained by the method outlined in the previous section, in the form

$$L(p) = \sum_{k=1}^9 a_k k! / (p+\alpha)^{k+1}$$

The function

$$R(\epsilon) = \sum_{k=1}^9 a_k \epsilon^k e^{-\alpha \epsilon}$$

is plotted for benzene in figure 5-2, and for hexadeutero-benzene in figure 5-4. The solutions $R(\epsilon)$ show the expected behaviour: an increase with increasing ϵ to a maximum in the $1100-1300\text{cm}^{-1}$ region, followed by a rapid decrease with increasing ϵ . The decrease is more rapid for hexadeutero-benzene than for benzene, which is in accordance with the observed isotope effect that radiationless processes are in general less efficient in deuterium substituted compounds than in the corresponding hydrogen compounds.

In this chapter a method has been outlined for the calculations of rates of radiationless processes in an isolated molecule in terms of fundamental properties of the molecule. A complete numerical calculation is not at present a practical proposition because of the lack of information

FIGURE 5-1: Laplace Fit for Benzene

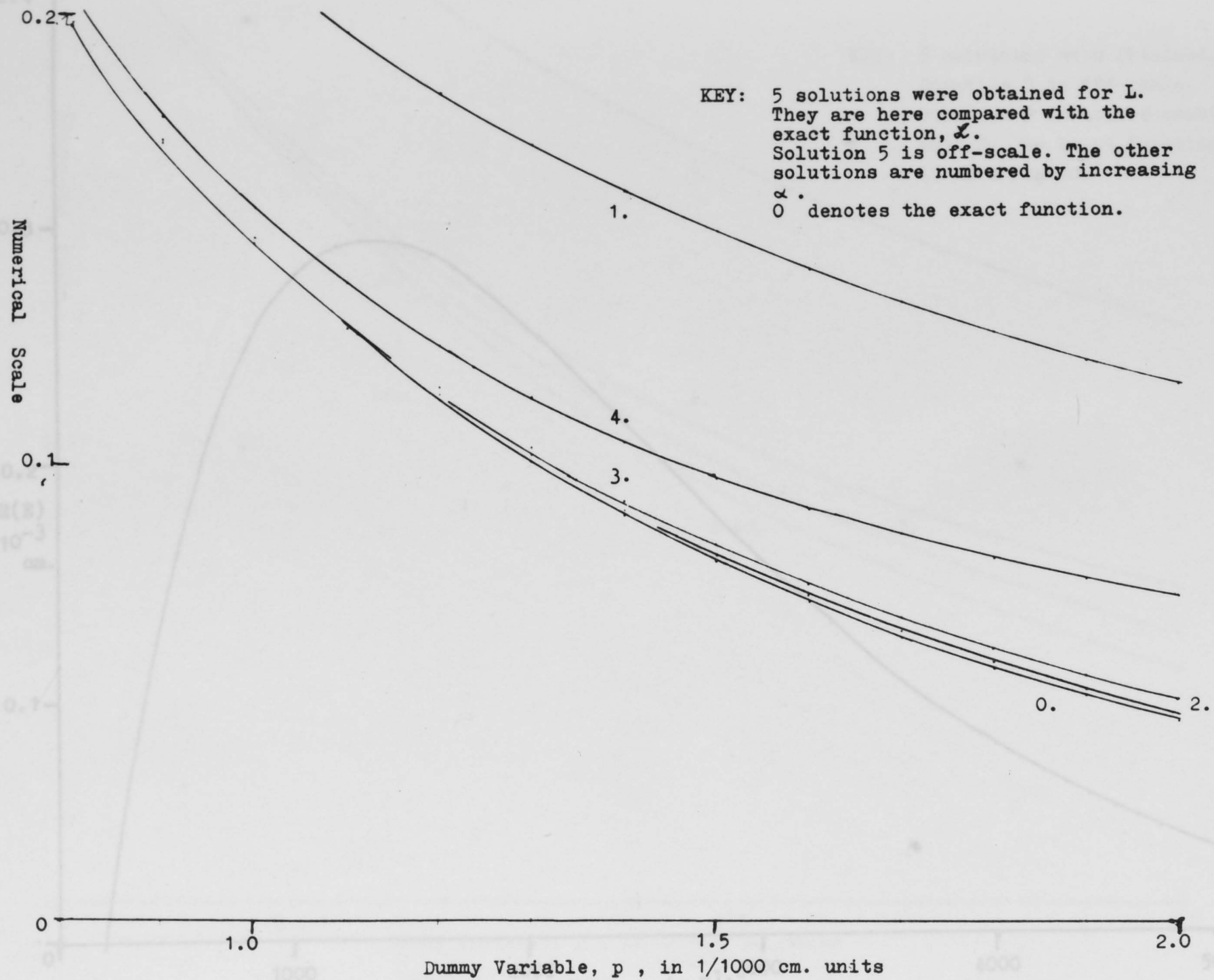


FIGURE 5-2: Approximate Laplace Inversion for Benzene

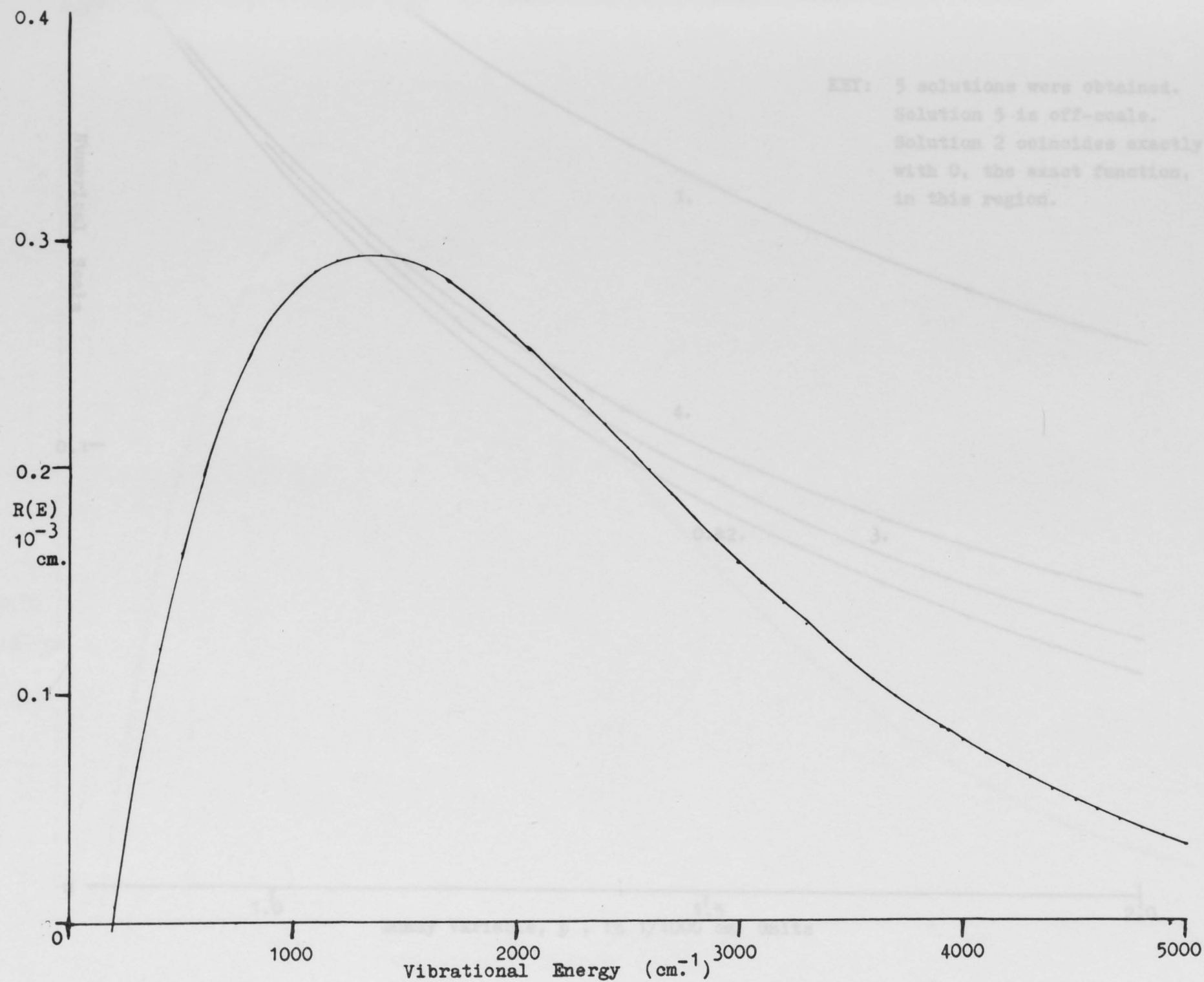


FIGURE 5-3: Laplace Fit for Perdeuterobenzene

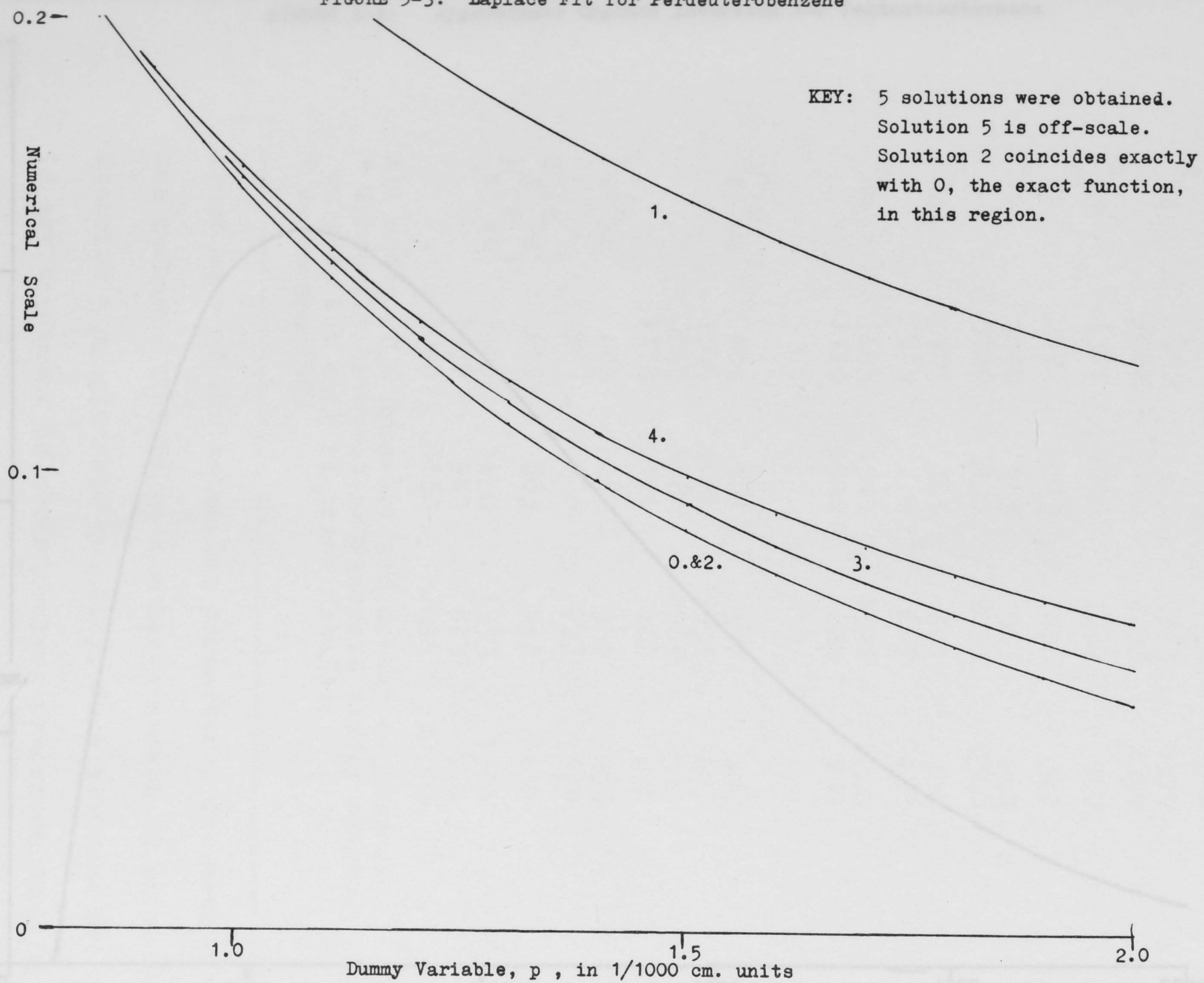


FIGURE 5-4: Approximate Laplace Inversion for Perdeutero benzene

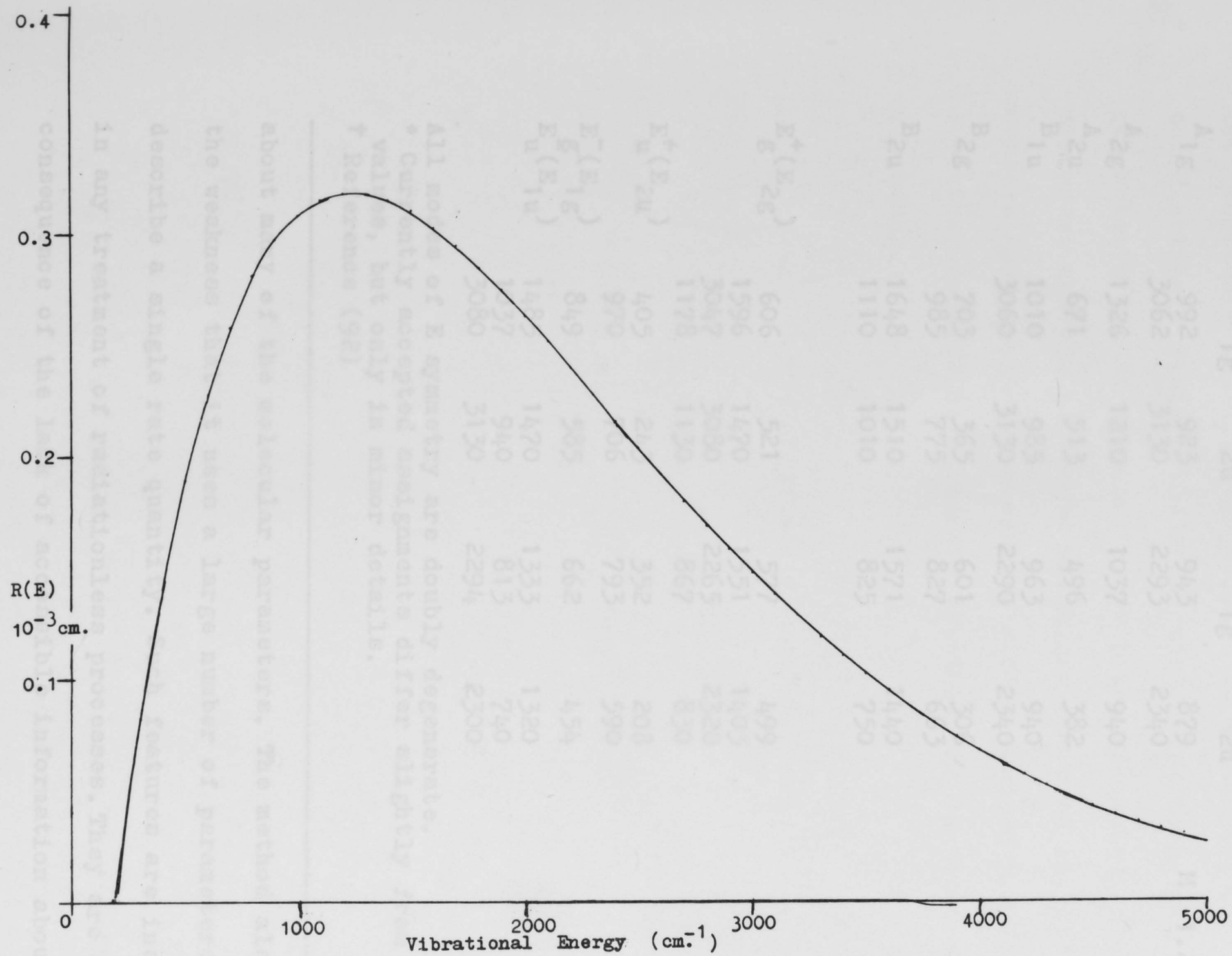


Table 5-1: Vibrational Frequencies in Benzene (in cm^{-1})

[Taken from Reference (91)*.]

Symmetry	Benzene		Perdeuterobenzene		Origin Shift
	$^1A_{1g}$	$^1B_{2u}$	$^1A_{1g}$	$^1B_{2u}$	
A_{1g}	992	923	943	879	M 1.23 [†]
	3062	3130	2293	2340	
A_{2g}	1326	1210	1037	940	
A_{2u}	671	513	496	382	
B_{1u}	1010	985	963	940	
	3060	3130	2290	2340	
B_{2g}	703	365	601	306	
	985	775	827	663	
B_{2u}	1648	1510	1571	1440	
	1110	1010	825	750	
$E_g^+(E_{2g})$	606	521	577	499	
	1596	1470	1551	1403	
	3047	3080	2265	2320	
	1178	1130	867	830	
$E_u^+(E_{2u})$	405	243	352	208	
	970	706	793	590	
$E_g^-(E_{1g})$	849	585	662	454	
$E_u^-(E_{1u})$	1485	1470	1333	1320	
	1037	940	813	740	
	3080	3130	2294	2300	

All modes of E symmetry are doubly degenerate.

* Currently accepted assignments differ slightly from these values, but only in minor details.

[†] Reference (92)

about many of the molecular parameters. The method also has the weakness that it uses a large number of parameters to describe a single rate quantity. Such features are inevitable in any treatment of radiationless processes. They are a direct consequence of the lack of accessible information about the processes and the electronic states which are involved in them. The model used is a more realistic one than that of

Bixon and Jortner, and disposes of the artificial properties of the simple model by allowing a diversity of matrix elements and level spacings. Moreover, no parameters are used which are not directly related to basic properties of the electronic states. The model thus helps to bridge the gap between the theoretical description of radiationless processes and the processes which are observed in real systems, and should be useful as a step towards providing a better description of some characteristic features of the processes.

For the calculation of the number of states in a vibrational manifold, and the quantities which are generally quoted for the density of states have been directly calculated from the formulas available. Often, insufficient account has been taken of the fact that many of the vibrational states in the final electronic state are unable to interact with the initial state for symmetry reasons. In this section the number of final states available for radiationless processes from a particular initial state is reestimated for a highly symmetrical system, the benzene molecule.

The benzene molecule belongs to the D_{6h} symmetry group. Its electronic states may only have the symmetry representations A_{1g} , A_{2g} , E_{1g} , E_{2g} , E_{3g} , and E_{4g} , as the electronic states of the molecule must be symmetric with respect to reflection in the molecular plane. The symmetry assignments of the symmetries of benzene electronic states are as follows:

CHAPTER 6: BENZENE - A NON-STATISTICAL EXAMPLE

(i) The Density of Effective States

In most of the published treatments of radiationless processes the density of final states is an important parameter. It may be used to obtain an estimate of coupling matrix elements from observed rates of radiationless processes⁷⁵, a comparison of rates from estimated values of matrix elements^{63,64}, or a justification of approximations made in the treatment⁷⁵. Various methods⁹³ have been devised for the calculation of the number of states in a vibrational manifold, and the quantities which are generally quoted for the density of states have been directly calculated from the formulae available. Often, insufficient account has been taken of the fact that many of the vibrational states in the final electronic state are unable to interact with the initial state for symmetry reasons. In this section the number of final states available for radiationless processes from a particular initial state is reestimated for a highly symmetrical system, the benzene molecule.

The benzene molecule belongs to the D_{6h} symmetry group. Its electronic states may only have the symmetry representations A_{1g} , A_{2g} , B_{1u} , B_{2u} , E_g , and E_u , as the electronic states of the molecule must be symmetric with respect to reflection in the molecular plane. The accepted assignments of the symmetries of benzene electronic states are as follows:

The ground state has A_{1g} symmetry; the lowest excited singlet is ${}^1B_{2u}$, the second ${}^1B_{1u}$ and the third ${}^1E_u^-$; the lowest triplet state is ${}^3B_{1u}$; other triplets are not so well characterized, but it is clear that ${}^3E_u^-$ and ${}^3B_{2u}$ states must also occur at low energy. Radiationless transitions between states of these symmetries will therefore be considered.

A particular matrix element, h_{if} , can be written by equation (7) of chapter 4 in the form

$$\begin{aligned} h_{if} &= \frac{\hbar^2}{2} \langle \phi_I | \sum_j \partial^2 / \partial q_j^2 | \phi_F \rangle \langle \chi^I(i) | \chi^F(f) \rangle \\ &\quad + \sum_j \hbar^2 \langle \phi_I | \partial / \partial q_j | \phi_F \rangle \langle \chi^I(i) | \partial / \partial q_j | \chi^F(f) \rangle \\ &= A \langle \chi^I(i) | \chi^F(f) \rangle + \sum_j B_j \langle \chi^I(i) | \partial / \partial q_j | \chi^F(f) \rangle \end{aligned}$$

For B_j to be non-zero, it is apparent that the product of the symmetry representations of q_j and ϕ_F must contain the symmetry representation of ϕ_I . The value of A can only be non-zero if the symmetry representation of ϕ_F contains that of ϕ_I . The allowed symmetries of q_j to give non-zero B_j for the various electronic state transitions are shown in table 6-1.

In the case of the benzene molecule, the characteristic frequencies of the modes which have non-zero B_j in the various electronic transitions are shown in table 6-2.

The vibrational parts of the matrix elements are now considered. The vibrational overlap functions in the harmonic approximation are determined by the origin shifts

Table 6-1: Allowed Symmetry of q_j for Non-zero B_j

ϕ_I	B_{2u}	B_{1u}	E_u^-
ϕ_F			
A_{1g}	B_{2u}	B_{1u}	E_u^-
B_{2u}	A_{1g}	A_{2g}	E_g^+
B_{1u}	A_{2g}	A_{1g}	E_g^+
E_u^-	E_g^-	E_g^-	E_g^+, A_{1g}, A_{2g}

Table 6-2: Frequencies* of Benzene Modes with Non-zero B_j

$B_{2u} \leftrightarrow A_{1g}$	(1648), (1110)
$B_{1u} \leftrightarrow A_{1g}$	(1010), (3060)
$E_u^- \leftrightarrow A_{1g}$	$2 \times (1485), 2 \times (1037), 2 \times (3080)$
$B_{2u} \leftrightarrow B_{2u}, B_{1u} \leftrightarrow B_{1u}, E_u^- \leftrightarrow E_u^-$	(992), (3062), A non-zero
$B_{2u} \leftrightarrow B_{1u}, E_u^- \leftrightarrow E_u^-$	(1326)
$E_u^- \leftrightarrow B_{2u}, E_u^- \leftrightarrow B_{1u}, E_u^- \leftrightarrow E_u^-$	$2 \times (606), 2 \times (1596), 2 \times (3047), 2 \times (1178)$

(* Ground state frequencies)

and the frequency changes between the electronic states involved. If the benzene molecule is to retain its D_{6h} symmetry in all of the electronic states considered, the only modes which can have an origin shift are the two A_{1g} modes. For modes which are not origin-shifted, the vibrational overlap function is non-zero only if there is an even change in the quantum number of the mode between the two states. Thus, for the vibrational overlap $\langle \chi^I(0) | \chi^F(f) \rangle$

to be non-zero, the requirement on the quantum numbers f_j is that f_j should be even for every mode except the A_{1g} modes, in which f_j can take any value. This is a much stronger condition than that imposed by Robinson⁹⁴, who rightly supposed that only vibrations whose total symmetry was A_{1g} could have non-zero overlap with the A_{1g} zero-vibrational level of another electronic state. The selection rule outlined above indicates that only a small proportion of A_{1g} states have non-zero vibrational overlaps, and that many A_{1g} vibrations have overlap integrals that are zero by symmetry.

The matrix elements involving the $\partial/\partial q_j$ operator with vibrational wavefunctions can be written as the sum of two vibrational overlap integrals, using equation (35) of chapter 5. These are the vibrational overlaps with the levels in which f_j is changed by ± 1 . For these vibrational overlaps to be non-zero $f_j \pm 1$ must be even (if i_j is even), and therefore f_j must be odd. This applies for all modes q_j not of A_{1g} symmetry. If the mode q_j is one of the A_{1g} modes, the conditions for non-zero matrix elements are the same as those outlined above for $\langle \chi^I(0) | \chi^F(f) \rangle$. If q_j is not an A_{1g} mode the conditions for non-zero matrix elements $\langle \chi^I(0) | \partial/\partial q_j | \chi^F(f) \rangle$ are that the vibrational quantum numbers in A_{1g} modes may take any value, the vibrational quantum number in the mode q_j must be odd, and all other vibrational quantum numbers must be even.

To compute the density of the final states f for which h_{if} is non-zero, these restrictions must be incorporated into the

calculation. To take account of modes which must have an even quantum number, it is sufficient merely to substitute double the value for the characteristic frequency of the mode each time it occurs in the formula. This includes the occurrence in the term $\sum_j \frac{1}{2} \nu_j$, as this term arises naturally in the counting procedure, and is not related to the zero point energy as such*. To take account of modes which must have an odd quantum number, the procedure is similar, except that in addition the value of E, the energy of the system above the zero-vibrational level, is diminished by the original value of the characteristic frequency of the mode, where it occurs in the formula. This scheme is appropriate regardless of the particular formula chosen to calculate the density of states.

In table 6-3 the density of states having non-zero vibrational overlap with the ground vibrational level of another electronic state is shown for benzene and deuterio-benzene, with the total density of states for comparison. Haarhof's⁴ method was used. The results were calculated from the equation

$$\rho(E) = \frac{(E + \frac{1}{2} \sum_j \nu_j)^{n-1}}{(n-1)! \prod_j \nu_j} \left[1 - \frac{1}{(1+\eta)^2} \right]^\beta \left[\left(1 + \frac{1}{1+\eta}\right) \left(1 + \frac{2}{\eta}\right)^{1/2} / e \right]^n \quad (2)$$

* A derivation of the "semiclassical" formula for the density of states is given in Appendix I, where this fact is clearly brought out.

Table 6-3: Density of States in Benzene

Energy above zero vibration (cm^{-1})	C_6H_6 Density of states		C_6D_6 Density of states	
	Total (cm)	Effective (cm)	Total (cm)	Effective (cm)
5000	948	1.2	1560	4.8
6000	4170	3.9	9230	17
7000	16600	11	47400	55
8000	60500	32	$2.17 \cdot 10^5$	164
9000	$2.06 \cdot 10^5$	81	$8.97 \cdot 10^5$	460
10000	$6.56 \cdot 10^5$	200	$3.41 \cdot 10^6$	1230
11000	$1.98 \cdot 10^6$	470	$1.21 \cdot 10^7$	3120
12000	$5.68 \cdot 10^6$	1065	$4.02 \cdot 10^7$	7600
13000	$1.56 \cdot 10^7$	2330	$1.26 \cdot 10^8$	17900
14000	$4.11 \cdot 10^7$	4960	$3.77 \cdot 10^8$	40600
15000	$1.04 \cdot 10^8$	10250	$1.07 \cdot 10^9$	89600
16000	$2.57 \cdot 10^8$	20700	$2.93 \cdot 10^9$	$1.92 \cdot 10^5$
17000	$6.12 \cdot 10^8$	40700	$7.70 \cdot 10^9$	$4.02 \cdot 10^5$
18000	$1.42 \cdot 10^9$	78600	$1.96 \cdot 10^{10}$	$8.23 \cdot 10^5$
19000	$3.19 \cdot 10^9$	149000	$4.81 \cdot 10^{10}$	$1.65 \cdot 10^6$
20000	$7.01 \cdot 10^9$	276000	$1.15 \cdot 10^{11}$	$3.23 \cdot 10^6$

where n is the number of normal modes. η is the ratio $E/(\frac{1}{2} \sum_j \nu_j)$, and β is a parameter related to the distribution of characteristic frequencies. Sets of degenerate states arising from contributions from the degenerate vibrational modes are counted as series of separate states. The vibrational frequencies used are those given in table 5-1 for the ground state of benzene. The outstanding feature of the table is the large difference in both cases between the total density of states and the density of states which have non-zero overlap with a particular state. Robinson⁹⁴ supposed that

about 1 state in 24 would have non-zero overlap, as this is the proportion of A_{1g} states, and that of these anything from about 1 in 20 to about 1 in 2 would have an effective overlap. Calculated from the selection rules outlined above, overlaps are non-zero in the energy region Robinson was considering ($\sim 9000\text{cm}^{-1}$) in only one state in 2500. The number of states with non-zero h_{if} can readily be obtained by considering table 6-2. The density of states with non-zero h_{if} , ρ_{Int} , depends on the symmetries of the electronic states involved in the interaction, and is given from the density of states with non-zero vibrational overlap, ρ_{Eff} , by the following relationships:

$$\text{for a } B_{2u} \leftrightarrow A_{1g} \text{ interaction } \rho_{\text{Int}}(E) = \rho_{\text{Eff}}(E-1648) + \rho_{\text{Eff}}(E-1110)$$

$$\text{for a } B_{1u} \leftrightarrow A_{1g} \text{ interaction } \rho_{\text{Int}}(E) = \rho_{\text{Eff}}(E-1010) + \rho_{\text{Eff}}(E-3060)$$

$$\begin{aligned} \text{for an } E_u^- \leftrightarrow A_{1g} \text{ interaction } \rho_{\text{Int}}(E) \\ = 2[\rho_{\text{Eff}}(E-1485) + \rho_{\text{Eff}}(E-1037) + \rho_{\text{Eff}}(E-3080)] \end{aligned}$$

$$\text{for a } B_{2u} \leftrightarrow B_{2u} \text{ or a } B_{1u} \leftrightarrow B_{1u} \text{ interaction } \rho_{\text{Int}}(E) = \rho_{\text{Eff}}(E)$$

$$\text{for a } B_{2u} \leftrightarrow B_{1u} \text{ interaction } \rho_{\text{Int}}(E) = \rho_{\text{Eff}}(E-1326)$$

$$\begin{aligned} \text{for an } E_u^- \leftrightarrow B_{2u} \text{ or an } E_u^- \leftrightarrow B_{1u} \text{ interaction } \rho_{\text{Int}}(E) \\ = 2[\rho_{\text{Eff}}(E-1596) + \rho_{\text{Eff}}(E-606) + \rho_{\text{Eff}}(E-1178) + \rho_{\text{Eff}}(E-3047)] \end{aligned}$$

$$\begin{aligned} \text{for an } E_u^- \leftrightarrow E_u^- \text{ interaction } \rho_{\text{Int}}(E) = \rho_{\text{Eff}}(E) + \rho_{\text{Eff}}(E-1326) + \\ \rho_{\text{Int}}(E) (E_u^- \leftrightarrow B_{1u}) \end{aligned}$$

Only in interactions involving E_u^- electronic states are the densities of accessible final states for a radiationless process significantly greater than the density of states in the final manifold having a non-zero overlap with the initial state, and even in these cases the increase is less than an order of magnitude.

The selection rules used for calculating ρ_{Eff} have been derived only within the framework of the harmonic approximation. Their application to real systems depends on the extent to which the selection rules persist beyond this approximation. It can be shown that the same rules apply for any functions which can be expressed in terms of products of functions for individual normal modes, even though the potential function in any mode may be anharmonic, and the normal mode basis may rotate in going from one electronic state to the other (provided the molecule retains its symmetry). The result arises naturally from the fact that the Hamiltonian must be a totally symmetric operator. The overlap integrals of the A_{1g} levels involving odd quantum number excitations of non-totally symmetric modes become non-zero only as the approximation of a product wavefunction over normal modes itself breaks down.

In the consideration of intramolecular radiationless processes the total density of states in the final manifold is usually quoted as the density of available final states⁷⁵. This does not seem appropriate to much of the discussion,

because of the great discrepancy between the total density of states and the density of available final states in the case of a highly symmetric molecule. The final states which are classified as unavailable may, however, have very small interactions with the initial state in some cases due to small correction terms to the product wavefunctions. They should probably be regarded as contributing to the dissipation of the electronic energy among the vibrational modes in the long time scale, while unimportant to the rate of the radiationless process. Also, in comparing systems of different symmetry the total density of states is probably a better comparison parameter than the density of states with non-zero overlap, as there will be a compensating tendency. The system which has few levels with non-zero overlap will tend to have a larger overlap integral for each of these levels than the less symmetrical system with a greater proportion of levels having non-zero overlap, if the systems have similar size and similar distortions between the electronic states considered.

(ii) The Importance of Individual Final States

When a highly symmetrical molecule such as benzene is considered, it is found that the density of states which have non-zero matrix elements for the radiationless coupling is considerably smaller than the total density of states in the vibrational manifold. The approximation of the delta-function

sum in equation (20) of chapter 5. with a smooth function can only reasonably be achieved in energy regions where a large number of terms in the sum occur in a narrow energy interval. Where the terms in the sum are sparsely spaced on the energy scale the rate function can only be obtained by individually replacing each delta-function with a peaked function of finite width. If the initial state occurs at an energy where effective vibrational levels of the final state are scarce, the rate of the radiationless decay of the state may depend on its exact energy relative to those of the vibrational states which have large interactions with it. In benzene this effect may be very important, because there is only a single mode (the 992 cm^{-1} A_{1g} mode) which is prominent in spectral progressions.

The smooth function $R(\epsilon)$ which was obtained to approximate $\text{Rate}(\epsilon)$ in the latter part of chapter 5 can only be a good approximation in the region where the effective levels are dense. The curve shown in figure 5-2, which rises to a maximum, and then falls away, in the low energy region, must be interpreted in the light of the fact that over 90% of the contribution in the vibrational energy region $0\text{-}3000\text{ cm}^{-1}$ comes from four individual levels: about 22% from the zero-vibrational level, 32% from the level with a single quantum excitation in the 992 cm^{-1} mode, $24\frac{1}{2}\%$ from the level with a two quantum excitation in this mode, and 13% from the level with a three quantum excitation in the mode. To obtain a

smooth curve for $R(\epsilon)$ in the form shown in figure 5-2 is to ascribe a half-width of several hundred reciprocal centimetres to the peaked functions which replace the delta-functions in the sum.

Two questions are raised by these considerations. The first is whether a minimum energy can be determined, above which the form of $R(\epsilon)$ in figure 5-2 (or a more accurate determination along similar lines) is a good description of the rate versus energy gap function for a pair of electronic states in benzene. The second is whether there is an alternative representation of the rate versus energy gap function in the low energy region.

The answer to the first question is obtained by examining the individual vibrational overlap integrals of various vibrational levels. The problem is not a scarcity of final states, as the density of allowed states in benzene is adequate for the radiationless transition mechanism to be operative, particularly in view of the fact that many of the forbidden levels may have very small, but finite coupling matrix elements. The real problem arises from the fact that the interaction matrix elements in the sum are completely dominated, at least at low energy, by a few levels with very large interactions. Calculations of individual vibrational overlaps in the harmonic approximation have been examined by Siebrand⁶⁸, who shows that whereas the overlap terms in modes which are essentially distorted between the two electronic

states decrease roughly exponentially with increasing quantum number, the terms in modes which are essentially displaced between the electronic states decrease somewhat faster.

In the benzene molecule, the A_{1g} mode at 992 cm^{-1} is a displaced mode with little distortion (between ${}^1B_{2u}$ and ${}^1A_{1g}$ electronic states, for which all of these results are calculated). Although the vibrational levels which have their excess vibrational energy stored exclusively in this mode have very large vibrational overlap integrals with the zero-vibrational level of the upper state for up to about nine or ten quanta, the vibrational overlap of levels which carry all of their excitation in this mode is smaller at higher energy than that of levels having about eight quanta of excitation in this mode, and two or four quanta of excitation in one of the highly distorted modes: B_{2g} at 703 cm^{-1} ; E_g^- at 849 cm^{-1} ; E_u^+ at 970 cm^{-1} ; or E_g^+ at 1596 cm^{-1} .

At still higher excess vibrational energy, levels involving excitation of the CH stretch modes with characteristic frequencies about 3000 cm^{-1} have the largest Franck-Condon factors. At high energy, the levels with the largest Franck-Condon factors involve about nine quanta of excitation in the 992 cm^{-1} A_{1g} mode, possibly two quanta in a highly distorted mode, and the balance of the energy in the CH stretch modes. This picture differs only in minor detail if anharmonicity is included in the calculation.

In table 6-4 the vibrational levels which have the largest Franck-Condon factors in their energy region are listed for energies between 7000 and 12000 cm^{-1} . The figures shown are valid only for the overlap of the zero-vibrational level of $^1B_{2u}$ with $^1A_{1g}$ vibrational levels. They are to be interpreted in a qualitative sense, as no account is taken of anharmonicity, and the figures depend rather critically on the exact values of the frequencies listed in table 5-1. It can be seen that in the region from 8000 to 12000 cm^{-1} the pure 992 cm^{-1} excitation levels lose their dominance, and at the same time a number of different types of level with similar magnitudes for their overlap integrals become prominent. The levels shown in table 6-4 include only those within a factor of e of the highest Franck-Condon factor in their energy region. A large number of terms become important in the sum in the region near 12000 cm^{-1} . It is apparent that somewhere in the region 8000-12000 cm^{-1} the peaked functions become sufficiently dense, and the prominent levels span the energy region sufficiently to produce a smooth curve similar to that shown in figure 5-2. The exact region where this happens depends on the width assigned to the peaked functions which are used to replace the delta-functions in equation (20) of chapter 5.

Table 6-4: Levels with Large Franck-Condon Factors

(7000-12000 cm^{-1})

992 cm^{-1} excitation only				992 and distorted mode				992 and CH stretch			
quanta energy $\ln \xi^2$				quanta 992 other energy $\ln \xi^2$				992 other energy $\ln \xi^2$			
8	7936	-8.11		6	A2	7358	-8.37				
				6	B2	7650	-8.76				
				6	C2	7892	-9.07				
				5	D2	8152	-10.37				
				7	A2	8350	-9.69				
9	8928	-9.61		7	B2	8642	-10.08				
				7	C2	8884	-10.39				
				6	D2	9144	-11.57				
				8	A2	9342	-11.11				
				8	B2	9634	-11.50				
10	9920	-11.19		8	C2	9876	-11.81				
								4	E2	10062	-13.56
								4	F2	10088	-12.83
								4	G2	10092	-12.87
								4	H2	10128	-12.75
11	10912	-12.83		7	D2	10136	-12.89				
				9	A2	10334	-12.61				
				9	B2	10626	-13.00				
				8	A4	10748	-13.70				
				9	C2	10868	-13.31	5	E2	11054	-14.61
				8	A2B2	11040	-14.50	5	F2	11080	-13.88
				8	D2	11128	-14.31	5	G2	11084	-13.92
				8	A2C2	11282	-14.81	5	H2	11120	-13.80
				10	A2	11326	-14.19				
				8	B4	11332	-14.88				
12	11904	-14.54		8	B2C2	11574	-15.20				
				10	B2	11618	-14.58				
				9	A4	11740	-15.20				
				8	C4	11816	-15.52				
				10	C2	11860	-14.89				

Other modes: A 703 cm^{-1} B_{2g} ; B 849 cm^{-1} E_g^- ; C 970 cm^{-1} E_u^+ ;
D 1596 cm^{-1} E_g^+ ; E 3047 cm^{-1} E_g^+ ; F 3060 cm^{-1} B_{1u} ;
G 3062 cm^{-1} A_{1g} ; H 3080 cm^{-1} E_u^- .

(iii) Alternative Approaches to the Rate Function

The second question raised in the last section concerns the possibility of alternative approaches to the function Rate described by equation (20) of chapter 5, in the intermediate energy region where the overall density of states is sufficient that the mechanism of intramolecular radiationless transitions is not greatly affected, but the interactions which govern the rate are dominated by a few sparsely spaced levels.

The method involving obtaining and inverting the Laplace transform of Rate is capable in principle of dealing with the situation. The difficulty is that in approximately inverting the Laplace transform a large number of terms would need to be included to give a reasonable description of the complex local structure which is a feature of the function in this energy region. However if too many terms are included the representation of the function becomes divergent, and functions which seek to reproduce the delta-function character of rapid variation, rather than the distribution of the terms in the sum, are obtained as approximations.

There appear to be two ways to avoid these difficulties. The first is a minor modification of the Laplace transform method. If the contributions to the Laplace transform from the levels with very large interaction matrix elements are subtracted from the exact Laplace transform before the approximate inversion is made, an approximation to the Rate

function can be obtained after numerical inversion which is a smooth function with several delta-function "spikes"

superimposed on it. A single term $h_{ig}^* h_{ig} \delta(E - \epsilon_g)$ in the sum

$$\text{Rate}(E) = \sum_f h_{if}^* h_{if} \delta(E - \epsilon_f)$$

will provide a contribution $h_{ig}^* h_{ig} e^{-\epsilon_g p}$ to the Laplace transform of the Rate function.

$$\mathcal{L}_p(\text{Rate}) = \sum_f h_{if}^* h_{if} e^{-\epsilon_f p}$$

$$\text{If } \mathcal{L}_p^1(\text{Rate}) = \mathcal{L}_p(\text{Rate}) - \sum_{j=1}^k h_{ij}^* h_{ij} e^{-\epsilon_j p}$$

is approximated in $\mathcal{L}_p(R^1)$, then Rate is approximated in

$$\text{Rate}(E) \simeq R^1(E) + \sum_{j=1}^k h_{ij}^* h_{ij} \delta(E - \epsilon_j) = R(E)$$

There are several disadvantages in this method. One is the problem of numerical accuracy, since the subtraction of the prominent terms from $\mathcal{L}_p(\text{Rate})$ leaves a residue, $\mathcal{L}_p^1(\text{Rate})$, which is much smaller, and has a correspondingly larger fractional error in its numerical evaluation. The other main problem is the interpretation of the function R in the immediate neighbourhood of one of the delta-function spikes. In these regions the only interpretation that can be made with confidence is that R^1 is a lower bound to Rate.

The alternative approach to the function Rate in the energy regions under consideration is simply to replace the delta-functions in the sum

$$\text{Rate}(E) = \sum_f h_{if}^* h_{if} \delta(E - \epsilon_f)$$

with peaked functions of an arbitrarily chosen width, and evaluate the sum directly^{*}. The difficulty in this approach is that of assessing the validity of a particular choice of width. The only criterion available is that the width should be sufficient to produce a slowly varying function as an approximation to Rate. The approach is a practical one because of the small numbers of states involved in large terms in the sum. Functions obtained by this method have been plotted for half-widths of 10 cm^{-1} for benzene in figures 6-1 and 6-2. The energy region 7000 cm^{-1} to 8000 cm^{-1} was chosen. The curves are probably greatly in error because of the lack of account of anharmonicity in their calculation, and should therefore be interpreted only as a qualitative indication of the type of local structure that is to be expected in this region. In table 6-5 the Franck-Condon factors of the most important vibrational levels in the region are tabulated. Figures 6-1 and 6-2 do seem to indicate that the rate of radiationless transitions could vary within about a factor of ten depending on the exact position on the energy scale of the final manifold, of the initial state, if it is in the 7000 cm^{-1} to 8000 cm^{-1} region. These results have been obtained using the Franck-Condon factors arising from the squares of the vibrational overlap functions. In

^{*} I am grateful to Dr. Len Dissado for this helpful suggestion.

FIGURE 6-2: BENZENE - FRANCK CONDON FACTOR DISTRIBUTION

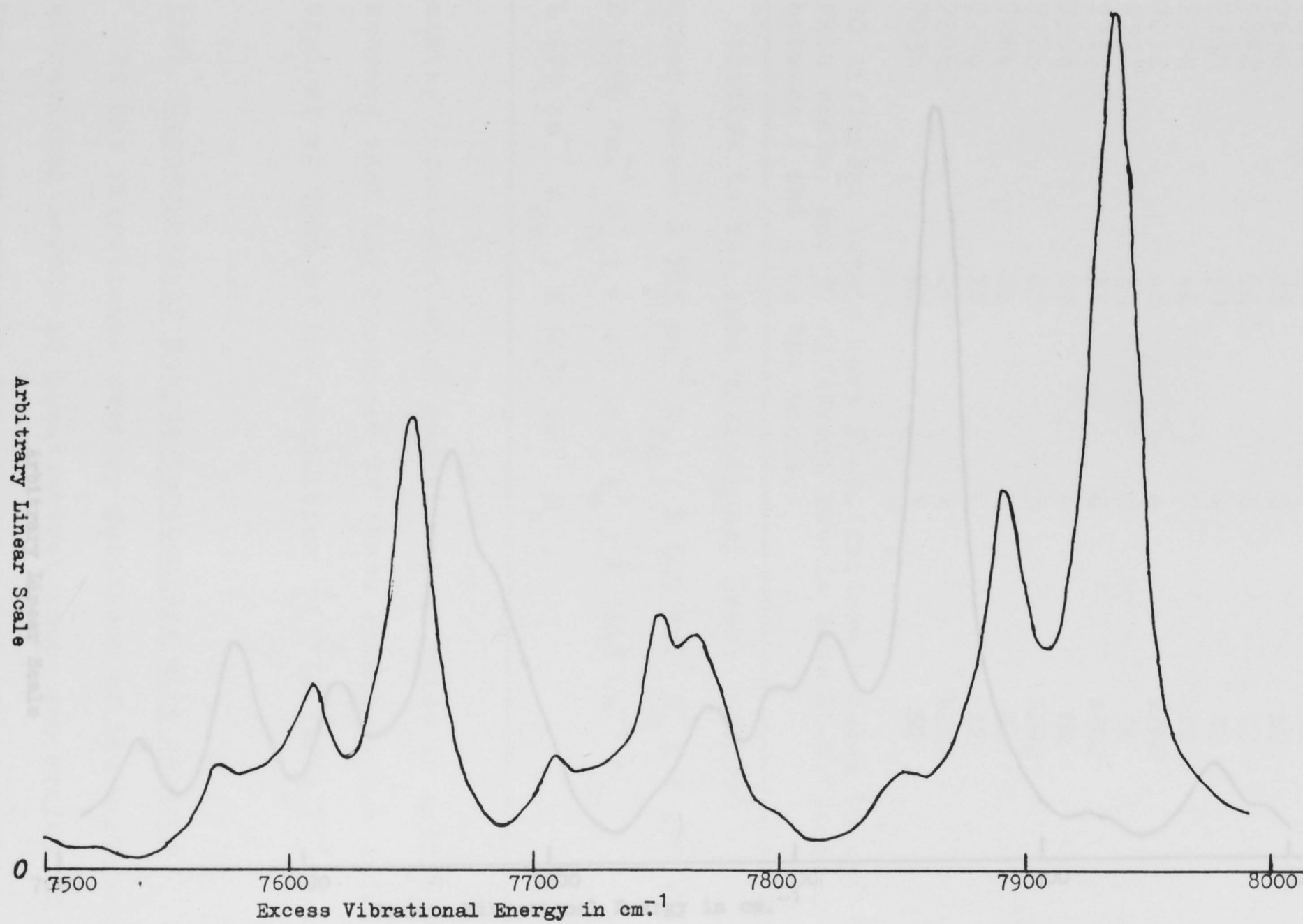
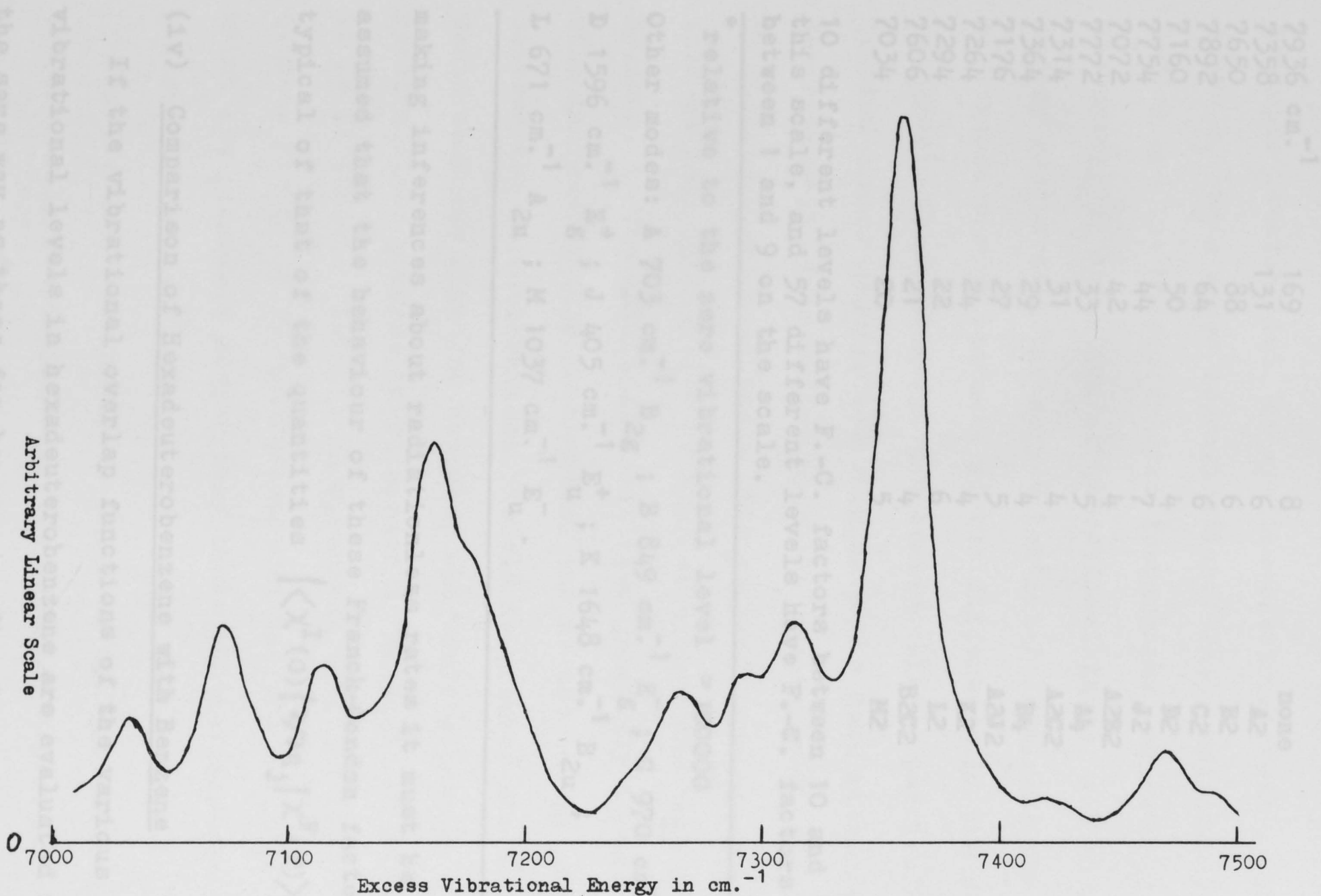


FIGURE 6-1: BENZENE - FRANCK CONDON FACTOR DISTRIBUTION



Approx. energy	Franck-Condon factor	Description
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7936 cm.⁻¹	169	8
7358	131	6
7650	88	6
7892	64	6
7160	50	6
7754	44	4
7072	42	4
7772	35	5
7314	31	4
7364	29	4
7176	27	4
7264	24	4
7294	22	4
7606	21	4
7034	20	4

10 different levels have F.-C. factors between 10 and 19 on this scale, and 57 different levels have F.-C. factors between 1 and 9 on the scale.

relative to the zero vibrational level.

Other modes: A 703 cm.⁻¹ B_{2g} ; B 849 cm.⁻¹ E_{2g} ; E 1596 cm.⁻¹ E_g ; J 405 cm.⁻¹ E_u ; K 1648 cm.⁻¹ B_{2g} ; L 671 cm.⁻¹ A_{2u} ; M 1037 cm.⁻¹ E_u.

Table 6-5: Prominent Vibrations in Benzene (7000-8000 cm^{-1})

Approx. energy	Franck-Condon factor*	Description		Degen- eracy
		992 quanta	Other quanta	
7936 cm^{-1}	169	8	none	1
7358	131	6	A2	1
7650	88	6	B2	2
7892	64	6	C2	2
7160	50	4	D2	2
7754	44	7	J2	2
7072	42	4	A2B2	2
7772	33	5	A4	1
7314	31	4	A2C2	2
7364	29	4	B4	3
7176	27	5	A2J2	4
7264	24	4	K2	1
7294	22	6	L2	1
7606	21	4	B2C2	4
7034	20	5	M2	2

10 different levels have F.-C. factors between 10 and 19 on this scale, and 57 different levels have F.-C. factors between 1 and 9 on the scale.

* relative to the zero vibrational level = 100000

Other modes: A 703 cm^{-1} B_{2g} ; B 849 cm^{-1} E_g^- ; C 970 cm^{-1} E_u^+ ;
D 1596 cm^{-1} E_g^+ ; J 405 cm^{-1} E_u^+ ; K 1648 cm^{-1} B_{2u} ;
L 671 cm^{-1} A_{2u} ; M 1037 cm^{-1} E_u^- .

making inferences about radiationless rates it must be assumed that the behaviour of these Franck-Condon factors is typical of that of the quantities $|\langle \chi^I(0) | \partial/\partial q_j | \chi^F(f) \rangle|^2$.

(iv) Comparison of Hexadeuterobenzene with Benzene

If the vibrational overlap functions of the various vibrational levels in hexadeuterobenzene are evaluated in the same way as those for benzene, a direct comparison can

be made. This gives some insight into the isotope effects in the rates of radiationless processes in benzene. The parameters ρ and M in the various modes are independent of isotopic substitution, as are the electronic matrix elements A and B_j (to a first approximation). The quantities which do differ are the characteristic frequencies, which will affect the energy of a particular vibrational level, and also the energy gap between the zero-vibrational levels of the two electronic states (because of the difference in the zero-point energies). Thus, although a vibration with a particular quantum number description will have the same matrix element describing its interaction with the zero-vibrational level of another electronic state, its excess vibrational energy will be less in the case of hexadeuterobenzene than in benzene. As the matrix elements tend generally to decrease with increasing quantum numbers, and as the energy gap between the zero-vibrational levels is greater for hexadeuterobenzene than for benzene, one would expect a radiationless process to be slower in hexadeuterobenzene than it is in benzene. This is in agreement with the observed quantum yields of phosphorescence in deuterated hydrocarbons, which are generally higher than those in the corresponding protonated species⁶⁷.

The question remains as to which of the vibrational modes are primarily responsible for the observed effect. Siebrand and Williams have, by analysis of the magnitude of the

observed isotope effect in a series of hydrocarbons, concluded that the CH and CD stretch modes govern the effect^{67,69,70}.

A convenient approach is to consider the magnitudes of the largest Franck-Condon factors in an energy region. For high energies this can be done in a simple way. For all of the modes which are distorted but undisplaced between the electronic states, the Franck-Condon factors decrease approximately exponentially with increasing quantum number. This is exactly true for the doubly degenerate modes, and a good approximation for the non-degenerate modes⁶⁸. It is possible therefore to describe an exponential "attenuation factor" per thousand reciprocal centimetres of vibrational energy stored in the mode. This cannot be done for the A_{1g} "ring breathing" mode, which is origin shifted. The Franck-Condon factor of a particular vibration is obtained by multiplying the Franck-Condon factor of the appropriate pure A_{1g} mode vibration by the attenuation factors appropriate to the energy stored in each of the other modes. Thus

$$|\langle \chi^I(0,0,0,\dots) | \chi^F(f_1, f_2, f_3, \dots) \rangle|^2 =$$

$$|\langle \chi^I(0,0,0,\dots) | \chi^F(f_1, 0, 0, \dots) \rangle|^2 \cdot \exp - \frac{1}{1000} (f_2 \nu_2 \alpha_2 + f_3 \nu_3 \alpha_3 + \dots)$$

where α_j are the attenuation factors, and 1 indexes the A_{1g} mode. Clearly the vibrations with the largest Franck-Condon factors have some energy stored in the A_{1g} mode, and most of the remainder stored in the modes with the lowest values of α .

The modes with low values of α are listed in table 6-6. It is apparent from the table that, whereas in benzene vibrations involving excitations of the CH stretch modes become dominant at high excitation energies, the vibrations with CD stretch modes excited in hexadeuterobenzene do not dominate, but have similar Franck-Condon factors to those of vibrations with the 1551 cm^{-1} ring stretching mode or the 793 cm^{-1} out-of-plane mode excited.

At low energies CH stretch and CD stretch modes are not important because of the large energy associated with a quantum in these modes. In these regions the vibrations with the largest Franck-Condon factors involve either excitation of the A_{1g} ring breathing mode alone, or excitations of the A_{1g} ring breathing mode associated with two or four quanta in the highly distorted low frequency modes. It is important to note, therefore, that the latter modes have large isotope effects, and the A_{1g} mode a small isotope effect, causing Franck-Condon factors to be generally larger for benzene than for hexadeuterobenzene in a particular energy neighbourhood. Moreover, the shift of the energy gap to a larger value in hexadeuterobenzene will also contribute markedly to an isotope effect in this region. At low energy values the Rate versus energy gap curve will be highly structured (as in figures 6-1 and 6-2), and isotope effects might have any of a large range of values, including the possibility of a small effect in the reverse direction. As an example of the effect

Table 6-6: Modes Involved in Levels with Large
Franck-Condon Factors

Mode	benzene		hexadeuterobenzene	
	ν	α	ν	α
B_{2g} ring pucker	703	2.13	601	2.50
E_g^- out of plane	849	2.00	662	2.56
E_u^+ out of plane	970	1.91	793	2.33
E_g^+ ring stretch	1596	1.94	1551	2.00
E_u^- CH stretch	3080	1.56	2296	2.10
B_{1u} CH stretch	3060	1.56	2290	2.10
A_{1g} CH stretch	3062	1.56	2293	2.10
E_g^+ CH stretch	3047	1.71	2265	2.30

predicted, the most prominent vibrations of energy about 22000 cm^{-1} have Franck-Condon factors about 250 times greater in benzene than in hexadeuterobenzene. The density of states, which is much higher in hexadeuterobenzene than in benzene, would tend to reduce this isotope factor. Isotope ratios of between 10 and 100 are typically observed for the comparison of radiationless triplet to ground state decay rates between protonated and fully deuterated hydrocarbons⁶⁷. The agreement is thus fairly good, particularly as anharmonicity has been completely neglected.

This view of the isotope effect is substantially in agreement with that of Hunt, McCoy, and Ross⁶⁵. The only

difference from Siebrand's view^{67,69} is that modes other than the CH stretch modes seem to play a more important part in this picture. Many of the levels with large Franck-Condon factors involve excitations of the highly distorted low frequency modes, and all involve excitations of the displaced ring breathing mode, as well as the CH stretch modes. In hexadeuterobenzene, in particular, the role of the CD stretch modes appears to be secondary to that of the E_g^+ CC stretching mode of frequency 1551 cm^{-1} . For electronic states with small energy separation, it is apparent that CH and CD stretching modes can play no important part, and any isotope effects which occur in this region must be governed by the frequency shifts of lower frequency modes.

CHAPTER 7: POSSIBLE REFINEMENTS OF THE MODEL

(i) A Vibrationally Excited Initial State

In the consideration of radiationless decay of electronically excited states of isolated molecules in chapter 5, it was assumed that the initial state produced by photon absorption was the ground vibrational level of the excited electronic state. While it would be possible to arrange an experiment so that this is the case, it has been more usual, in the experimental studies that have been done, to use an appropriate mercury line emission. The frequency of this emission is such that the system must gain, in a typical case, about a thousand reciprocal centimetres of vibrational excitation energy, as well as undergoing electronic excitation, in order to absorb a photon. This raises the question of the dependence of radiationless rates on the excess vibrational energy in the initial state, or, more properly, on the quantum description of the vibrational wavefunction of the initial state. In particular, for considering the decay of excited electronic states which have electronically forbidden, but vibronically allowed radiative interactions with the ground state, the initial state considered in the description of the radiationless process is necessarily vibrationally excited (in the absence of environmental interactions which could allow fast vibrational relaxation).

Equation (46) of chapter 5 was derived assuming zero quantum numbers in the initial state. Alternative expressions

can be obtained if the quantum number of the initial state is non-zero. Where $f_j(1,n)$ is used to denote the overlap integral in a particular mode ($f_j(1,n) = \langle \chi_{j1}^I | \chi_{jn}^F \rangle$) the Laplace transform with respect to final state energy of the summed squares of the vibrational overlap functions is given by (equation 34, chapter 5)

$$\mathcal{L}(p) = \prod_j \left[\sum_n f_j^2(1,n) e^{-n\nu_j p} \right] \quad (1)$$

In equation (40) of chapter 5, the sum is given for $l=0$.

$$\sum_n f^2(0,n) y^n = \sqrt{\frac{1-\rho^2}{1-\rho^2 y^2}} e^{-M^2(1-y)/(1-\rho y)}$$

To deal with the vibrationally excited initial state, it is necessary to know the values of the sum for l values other than zero. These can be obtained, but they are expressions which increase rapidly in complexity with increasing l , and their derivation is a tedious algebraic problem. Two examples are given here.

$$\sum_n f^2(1,n) y^n = \sqrt{\frac{1-\rho^2}{1-\rho^2 y^2}} e^{-M^2(\frac{1-y}{1-\rho y})} \left[\frac{y(1-\rho^2)}{1-\rho^2 y^2} + M^2(1+\rho)\left(\frac{1-y}{1-\rho y}\right)^2 \right] \quad (2)$$

$$\sum_n f^2(2,n) y^n = \sqrt{\frac{1-\rho^2}{1-\rho^2 y^2}} \left[\frac{y^2(1-\rho^2)^2 + \frac{1}{2}\rho^2(1-y^2)^2}{(1-\rho^2 y^2)^2} \right] \quad (3)$$

when $M=0$. These two formulae cover many practical cases of vibrationally excited initial states whose decay is to be studied. The other cases could be covered by an infinite string of increasingly complicated formulae, or possibly by

recurrence relations. There is, however, a more concise formula which enables them to be generated. The sum which is evaluated is the double sum

$$\sum_{l=1}^{\infty} \sum_{n=1}^{\infty} f^2(l,n) y^n x^l = \sqrt{\frac{1-\rho^2}{1-xy-\rho^2(x-y)^2}} \exp \frac{-M^2(1-y)(1-x)}{1-xy+\rho x-\rho y} \quad (4)$$

This is an extremely valuable result. Any of the sums of the form in (1) can be evaluated from it directly (if not simply) by the use of the formula for the coefficient of x^l

$$\sum_n f^2(l,n) y^n = \frac{1}{l!} \frac{\partial^l}{\partial x^l} \left[\sum_n \sum_l f^2(l,n) y^n x^l \right]_{x=0} \quad (5)$$

The formula in itself is also immediately useful. The distribution of Franck-Condon factors with a particular initial state as a function of vibrational energy in the final manifold has been considered in the form

$$S(\epsilon) = \frac{d}{d\epsilon} \sum_f^{\epsilon_f \leq \epsilon} \left| \langle \chi^I(i_1, i_2, i_3, \dots) | \chi^F(f_1, f_2, f_3, \dots) \rangle \right|^2 \quad (6)$$

and the Laplace transform of S has been shown to be

$$\mathcal{L}_p(S) = \pi \left[\sum_j f_j^2(i_j, n) e^{-n\nu_j p} \right] \quad (1)$$

It is now possible to consider the variation of S with the excess vibrational energy of the initial state also. If ϵ is replaced with e_f , a continuous variable representing the excess vibrational energy in the final electronic manifold, and e_i represents the excess vibrational energy in the initial electronic manifold, then S may be defined as a function of the two variables e_i and e_f .

$$S(e_i, e_f) = \frac{\partial^2}{\partial e_i \partial e_f} \sum_i^{\varepsilon_i \leq e_i} \sum_f^{\varepsilon_f \leq e_f} |\langle \chi^I(i) | \chi^F(f) \rangle|^2 \quad (7)$$

and a double Laplace transform of S is readily available in the form

$$\begin{aligned} \mathcal{L}_{p_i} \mathcal{L}_{p_f}(S) &= \prod_j \left[\sum_n \sum_l f_j^{2(1,n)} e^{-n\nu_j^F p_f} e^{-l\nu_j^I p_i} \right] \\ &= \prod_j \left[\sqrt{\frac{1 - \rho^2}{1 - xy - \rho^2(x-y)^2}} \exp \frac{-M^2(1-y)(1-x)}{1 - xy + \rho x - \rho y} \right] \end{aligned} \quad (8)$$

where ρ, x, y , and M all depend on j . x_j is given by $\exp(-\nu_j^I p_i)$ and y_j by $\exp(-\nu_j^F p_f)$.

The radiationless decay of a Boltzmann distribution of initial levels into the final manifold is also readily described. One simply replaces the variable p_i with the constant $1/kT$ in (8), and treats the resulting expression as a single Laplace transform in the dummy variable p_f of a function $S_1(e_f)$. This function is equivalent to the Boltzmann average of $S(e_i, e_f)$ over the initial energy variable, e_i . The result is not of great practical value in a consideration of the intramolecular vibrations of large molecules however, because kT is typically much smaller than ν_j^I , and vibrationally excited initial states are not appreciably populated.

The results in equations (2) to (5) and (8) do appear to deal with the problem of a vibrationally excited initial state, and their fuller exploration may provide valuable

information. Among other things, they should be capable of predicting the sensitivity of the rates of radiationless decay of an electronic state to the amount of excess vibrational energy in the state. Slight modifications will occur in the form of (8) when the correct vibrational matrix elements are used, rather than simple vibrational overlap integrals.

(ii) Inclusion of Second Order Coupling

In the model of radiationless processes the simplified view has been taken that only the two electronic states are involved. In real molecular systems there are other electronic states which are coupled both to the initial and the final electronic states. When this situation exists, there are second order corrections to the matrix element which governs the rate of radiationless decay. These are given in equations (21) to (25) of chapter 5. The largest of the correction terms has the form

$$\frac{2\pi}{h} \frac{d}{d\varepsilon} \left[\sum_f^{\varepsilon > \varepsilon_f} 2 h_{if} \left(\sum_k \frac{h_{ik} h_{kf}}{\varepsilon_i - \varepsilon_k} \right) \right]$$

where it has been assumed for convenience that the matrix elements of h are real. It is not apparent whether this term is negligible in all practical cases, or, if it is not negligible, for which cases it is likely to be important.

The term can add a positive or negative correction to the Rate function. This can be most easily seen by considering

the case where the sum over the levels k is dominated by one term arising from a level with $\epsilon_k \approx \epsilon_i$. In this case a small variation in ϵ_k does not markedly affect h_{if} , h_{ik} , or h_{kf} , but it can easily change the sign of $\epsilon_i - \epsilon_k$, and therefore of the whole correction.

A scheme for evaluating this correction term has not been devised. One approach which might prove feasible would be to treat the sum over the states k analogously to the treatment of the first order term. Thus

$$\sum_k \frac{h_{ik} h_{kf}}{\epsilon_i - \epsilon_k} = \int_0^\infty \frac{\sum_k h_{ik} h_{kf} \delta(e_k - \epsilon_k)}{\epsilon_i - e_k} de_k \quad (9)$$

If the expression $\sum_k h_{ik} h_{kf} \delta(e_k - \epsilon_k)$ could be evaluated by a procedure similar to the procedure used to obtain the very similar expression which arises in equation (20) of chapter 5 the definite integral in (9) can be calculated, and the correction term obtained from this quantity. Severe difficulties are to be expected, however, unless the sum and the definite integral can both be obtained in closed algebraic form, since both must be expressed explicitly as functions of the state indexed f in order to proceed with the evaluation of the correction term.

The experimental observations appear to be explained by the first order model. At low energy gap between the zero-vibrational levels of the electronic states, the density of states does not appear to become too small to allow a rapid radiationless process to be governed by the first order term

until the energy gap becomes very small indeed. In any case the rates of radiationless processes predicted by the first order theory become very uncertain at low energy gap, because of the importance of local structure in the Rate versus energy curve. Any correction term in this type of situation would not give greater insight into the rates of radiationless processes, as the theory can not make definite predictions in any case. Little more can be said in the absence of an evaluation of the second order term. If, however, the second order term were found to be significant in some cases of practical interest, higher order terms would also need to be evaluated, as the convergence of the perturbation expansion is called into question.

(iii) The Treatment of Anharmonicity

The evaluation of the Rate versus energy function in chapter 5 relies very heavily on the harmonic approximation in deriving specific forms for the vibrational matrix elements. It is known that the harmonic approximation is inadequate for many purposes, and particularly so in describing states with high vibrational energy. It is apparent that for motion along any normal coordinate the potential function must either asymptotically approach a finite maximum (equivalent to bond breaking) or effectively approach infinity at a finite position (equivalent to the close approach of atomic cores) as the displacement along the normal coordinate from the

origin (at the potential minimum) increases. Moreover, there is also a tendency for some modes to have deviations from harmonicity even near the potential minimum: out-of-plane modes typically have broadened potential wells, and sometimes even tend to have double minima.

The model for radiationless transitions developed in chapter 5 may thus be subject to a fairly large error because of its use of harmonic wavefunctions in describing final vibronic levels with high vibrational energies such that the harmonic approximation is not a good approximation. The possibility of including some sort of consideration of anharmonicities in the treatment should be examined.

Anharmonicity in molecular vibrations has generally been treated only for diatomic molecules or for small, highly symmetric molecules. The problem in these cases has involved the replacement of the quadratic potential function with a function that better describes the potential in the mode, and the calculation of the eigenvalues, the oscillator wavefunctions, or the overlap integrals, as required. In larger molecular systems, however, there are more complex manifestations of anharmonicity. The effective potential function in a particular normal mode is not truly independent of the other nuclear coordinates, and in cases where there is more than one mode of a particular symmetry representation, the minimum of the effective potential function may shift from the zero chosen for the mode, depending on the coordinate in

another mode of the same symmetry. In these circumstances the approximation of a product wavefunction over normal modes breaks down, and the description of the vibrational states becomes very complicated.

The relative importance of the two types of anharmonicity in large molecular systems is not known. An estimate can be made from the measured spectrum of benzene. The differences in the energy intervals along a progression in the spectrum are, to some extent, a measure of the anharmonicity within the A_{1g} mode forming the progression. The differences in the energy intervals between a particular pair of progression members in different progressions should give a similar measure of the anharmonicity which couples different vibrational modes to the A_{1g} mode. Although the data are difficult to interpret with the precision required, the tabulation of Garforth and Ingold⁹¹ suggests that the two effects have a similar magnitude. Garforth and Ingold comment on the breakdown of the high degeneracy expected for vibrational levels involving several quanta in E symmetry vibrational modes. This, too, is an indication of the importance of the anharmonicity effect which couples the different modes.

The model of chapter 5 seems unlikely to be amenable to explicit consideration of either type of anharmonicity, even as a perturbation effect. The simplicity of the expressions obtained depended on the fact that the energy eigenvalues

formed evenly spaced progressions, so that the Laplace transform could be factorized into an expression for each normal mode, and these expressions were power series which could be reduced to a closed algebraic form. Any explicit consideration of coupling between normal modes would prevent factorization of the Laplace transform, while an anharmonic potential function in a normal mode would lead to a sum which was not a power series. Either effect would largely destroy the value of the approach.

While there appears to be no place for the explicit inclusion of anharmonicity in a modification of the approach, its inclusion in an empirical fashion may add to the usefulness of the model. The type of modification that may be envisaged would involve either using slightly altered values for initial parameters, or an empirical relation to correct the values predicted by the treatment which neglects anharmonicity. The formulation of such modifications would require extensive numerical experience of the method, and many direct comparisons of theory and experiment. Anharmonicity thus remains for the present an uncertainty in the predictions of the method.

(iv) Electronic Matrix Elements

The treatment of radiationless processes in this thesis has so far ignored the values of the electronic parts of the coupling matrix elements. The method would be considerably

enhanced if absolute values could be assigned to these quantities. Perturbation expansions are available for the matrix elements⁷⁵, and their evaluation is within the bounds of feasibility. Long and detailed molecular orbital calculations would be required, however, and the accuracy of the result may prove difficult to estimate. The evaluation of relative sizes of the different electronic matrix elements which govern the different vibrational terms is probably a more practical proposition.

For the benzene molecule a very crude estimate of the relative importance of the different terms may be obtained in a simple manner in some cases. It is supposed that the transition under consideration is one which has non-zero B_j for modes of only one symmetry species, which is a non-degenerate species. This applies to all interactions between A_{1g} , B_{2u} , and B_{1u} electronic states. Transitions between these states are allowed by matrix elements B_j for q_j having symmetry A_{1g} , A_{2g} , B_{1u} , or B_{2u} . There is only one mode of A_{2g} symmetry. For the other three symmetries there are two matrix elements B_j involved. Both of the modes in each species involve motion of carbon and hydrogen atoms along the same axes (radial for A_{1g} and B_{1u} ; tangential in-plane for B_{2u}). While one mode involves an in-phase motion of carbon and hydrogen atoms, the other involves an orthogonal out-of-phase motion. A basis of two orthogonal coordinates is chosen for each symmetry species. x_c is a mass-normalized coordinate

involving motions of the carbon atoms only, in a manner appropriate to the symmetry species. x_H is a similar coordinate involving motions of the hydrogen atoms only. The normal coordinates may be directly calculated using the characteristic frequencies of the benzene and perdeutero-benzene molecules. They are given approximately by:

$$\begin{aligned}
 q_1(A_{1g}) &= 0.946 x_C(A_{1g}) + 0.324 x_H(A_{1g}) & \nu &= 992 \text{ cm}^{-1} \\
 q_2(A_{1g}) &= -0.324 x_C(A_{1g}) + 0.946 x_H(A_{1g}) & \nu &= 3062 \\
 q_1(B_{1u}) &= 0.948 x_C(B_{1u}) + 0.319 x_H(B_{1u}) & \nu &= 1010 \\
 q_2(B_{1u}) &= -0.319 x_C(B_{1u}) + 0.948 x_H(B_{1u}) & \nu &= 3060 \\
 q_1(B_{2u}) &= 0.848 x_C(B_{2u}) + 0.531 x_H(B_{2u}) & \nu &= 1648 \\
 q_2(B_{2u}) &= -0.531 x_C(B_{2u}) + 0.848 x_H(B_{2u}) & \nu &= 1110
 \end{aligned}$$

The corresponding coefficients for perdeutero-benzene are 0.881 and 0.473 for A_{1g} , 0.884 and 0.468 for B_{1u} , and 0.962 and 0.275 for B_{2u} .

At this point an assumption is made about the electronic part of the matrix elements. Two alternative assumptions are explored here. The first is to suppose that the positions of the hydrogen atoms have little influence on the matrix elements between the electronic states, since the matrix elements will be governed by the valence electrons, and primarily by the pi electrons, as the sigma structure does not differ greatly between the two electronic states. In this case a convenient simplification can be made.

$$\langle \phi^I | \partial / \partial x_H | \phi^F \rangle = 0 ; \quad \langle \phi^I | \partial / \partial x_C | \phi^F \rangle = K .$$

and therefore

$$\langle \phi^I | \partial / \partial q_k | \phi^F \rangle = K . \partial q_k / \partial x_C$$

In this approximation the following results are obtained.

$B(992 \text{ cm}^{-1}) = 2.92 B(3062 \text{ cm}^{-1})$	$(C_6H_6 : A_{1g})$
$B(1010 \text{ cm}^{-1}) = 2.97 B(3060 \text{ cm}^{-1})$	$(C_6H_6 : B_{1u})$
$B(1648 \text{ cm}^{-1}) = 1.60 B(1110 \text{ cm}^{-1})$	$(C_6H_6 : B_{2u})$
$B(943 \text{ cm}^{-1}) = 1.86 B(2293 \text{ cm}^{-1})$	$(C_6D_6 : A_{1g})$
$B(963 \text{ cm}^{-1}) = 1.89 B(2290 \text{ cm}^{-1})$	$(C_6D_6 : B_{1u})$
$B(1571 \text{ cm}^{-1}) = 3.50 B(825 \text{ cm}^{-1})$	$(C_6D_6 : B_{2u})$

The alternative approximation is to consider a pair of coordinates which have slightly different orientations. One coordinate is chosen so as to represent a concerted movement of each CH unit, leaving the CH bond as little altered as possible. The other involves motions within CH units which leave their centres of mass (or in the case of tangential motions, their centres of inertia about the molecular centre) stationary. For the A_{1g} and B_{1u} symmetry species, which involve radial motions, these coordinates are given by

$$\left. \begin{aligned} x_{CH} &= \sqrt{12/13} x_C + \sqrt{1/13} x_H \\ x_{C-H} &= -\sqrt{1/13} x_C + \sqrt{12/13} x_H \end{aligned} \right\} \text{ for } C_6H_6$$

$$\left. \begin{aligned} x_{CD} &= \sqrt{6/7} x_C + \sqrt{1/7} x_D \\ x_{C-D} &= -\sqrt{1/7} x_C + \sqrt{6/7} x_D \end{aligned} \right\} \text{ for } C_6D_6$$

For the B_{2u} modes which involve tangential motion the motion of the H must be weighted over that of the C by their relative distances from the molecular centre. This ensures that the two atoms remain colinear with the molecular centre in the CH motion. The weighting factor is close to $\sqrt{3}$.

$$x_{CH} = \sqrt{4/5} x_C + \sqrt{1/5} x_H$$

$$x_{CD} = \sqrt{2/3} x_C + \sqrt{1/3} x_D$$

with similar expressions for x_{C-H} and x_{C-D} . The approximation is made

$$\langle \phi^I | \partial / \partial x_{C-H} | \phi^F \rangle = 0 ; \quad \langle \phi^I | \partial / \partial x_{CH} | \phi^F \rangle = K'$$

leading to

$$\langle \phi^I | \partial / \partial q_k | \phi^F \rangle = K' \partial q_k / \partial x_{CH}$$

The results of this approximation are

$B(992) = 20 B(3062)$	$(C_6H_6 : A_{1g})$
$B(1010) = 23 B(3060)$	$(C_6H_6 : B_{1u})$
$B(1648) = 10.4 B(1110)$	$(C_6H_6 : B_{2u})$
$B(943) = 9.5 B(2293)$	$(C_6D_6 : A_{1g})$
$B(963) = 10.0 B(2290)$	$(C_6D_6 : B_{1u})$
$B(1571) = -2.9 B(825)$	$(C_6D_6 : B_{2u})$

There are large discrepancies between the two methods, although they do agree qualitatively. The results do suggest

that in these symmetry species in benzene, the matrix element of the mode involving primarily hydrogen motions is considerably smaller than that of the mode involving primarily carbon motions, but probably not sufficiently to consider the former negligible.

This type of approach is limited to highly symmetrical systems like benzene. A more detailed calculation is necessary to establish a comparison between the matrix elements in less symmetrical systems. A comparison which must normally be made between the matrix elements arising from radial and tangential motions of the carbon atoms has been avoided in this case because modes involving these motions have different symmetry species.

(v) Conclusion

The model for the description of intramolecular radiationless processes which has been explored through the last three chapters appears to be a very useful one. Its great advantage is its relation of the processes to basic molecular quantities without recourse to empirical parameters. Its disadvantages arise from the complexity of the systems studied, and the lack of precise information about the electronic states of large molecules. Similar difficulties to those encountered here appear to be inevitable in any similar treatment of the processes.

In this chapter the possibilities for refinement within

the general framework of the approach have been considered. Several modifications do appear to be possible, and may become useful in the light of additional experimental information, or of reliable calculations. The most fruitful area for the further exploration of the method at present appears to be in the devising of a scheme for calculating the electronic part of the interaction matrix elements.

To include anharmonicity which, in a complex molecule, can only be specified by a large number of unrelated parameters (most of which are not at present experimentally accessible) will be difficult in any theory. Its treatment in the present theory in an explicit manner does not at present seem practicable.

APPENDIX : THE SEMICLASSICAL FORMULA FOR THE DENSITY OF STATES

The number of eigenvalues in unit energy interval of a set of orthogonal harmonic oscillators is a problem which has received considerable attention because of its application to the vibrational energy levels of large molecules. Many formulae, of widely varying complexity and accuracy have been devised to give values to this quantity. In this section a novel derivation of the "semiclassical" formula is presented, in order to clarify the modifications which should be made in obtaining an "effective" density of states formula which would not count some of the states because of quantum selection rules which may be applicable in a particular problem. The semiclassical formula is one of the more frequently used approximations, as it is a suitable compromise between simplicity and accuracy in many applications.

The eigenvalues of an assembly of non-interacting harmonic oscillators are given by $E_k = \sum_j^N n_{kj} \nu_j$, where N is the number of oscillators, ν_j is the characteristic energy of the j th. oscillator, and n_{kj} is the quantum number of the j th. oscillator in the level indexed k . The energy zero has been taken arbitrarily as the energy of the zero quantum level; it could equally well have been chosen at the potential minimum - an equivalent result should be obtained. The initial step in the derivation is to count the total number of levels with eigenvalues less than an arbitrary energy, E . The states may

conveniently be described as the non-negative lattice points in quantum number space. If each quantum number n_j is supposed to be a continuous variable, the eigenfunctions of the system may be described by plotting the values of n_j along a set of orthogonal axes in an N -dimensional space. Thus the state ϕ_k with eigenvalue E_k is represented by a point in the space whose position vector is given by $\underline{r}_k = \sum_j n_{kj} \underline{u}_j$, where \underline{u}_j is the unit vector corresponding to n_j . As n_{kj} has a non-negative integral value for any eigenstate ϕ_k , it can be seen that all eigenstates are represented as non-negative integral lattice points in the space.

The levels with eigenvalues less than E are those contained in the part of the space $\sum_j \nu_j n_j < E$. The number of such levels is the same as the number of integral lattice points contained in the right simplex defined by

$$n_j \geq 0, \forall j. \quad \sum_j \nu_j n_j < E.$$

A first approximation to this number is the contents of the right simplex. The orthogonal edges of the right simplex have lengths E/ν_j . The contents is therefore given by

$$P(E) = \frac{1}{N!} \prod_{j=1}^N (E/\nu_j)$$

The condition for this quantity to be a good approximation is that the number of lattice points on the orthogonal hypersurfaces should be small with respect to the total

number of lattice points. This is equivalent to the condition that the number of levels with any zero quantum number is small compared to the total number of levels. This is clearly only applicable for small N , and large E , and is obviously a very poor approximation for typical values of N and E which are of interest in studying the vibrational levels of large molecules. Differentiation of $P(E)$ with respect to E gives the "classical" expression for the density of states: a notoriously poor approximation which is usually many orders of magnitude too small.

$$\rho_c(E) = E^{N-1} / (N-1)! \prod_{j=1}^N \nu_j$$

A better approximation can be obtained in the following way. Each point is allowed to expand into a unit hypercube centred on the original point. The number of states is then clearly equal to the total contents of the stack of hypercubes. The contents of this stack is very well approximated by the contents of a different simplex.

$$n_j \geq -\frac{1}{2}, \forall j; \quad \sum_j \nu_j n_j < E.$$

This simplex accounts accurately for the contents of the hypercubes representing the zero-quantum states, and its only error is associated with its representation of the contents of the hypercubes along the non-orthogonal hypersurface of the simplex. The length of each orthogonal edge of this simplex is given by $(E + \frac{1}{2} \sum_j \nu_j) / \nu_k$, and so the contents is

given by

$$P(E) = (E + \frac{1}{2} \sum_j \nu_j)^N / N! \prod_k \nu_k$$

and the density of states by

$$\rho_{SC}(E) = (E + \frac{1}{2} \sum_j \nu_j)^{N-1} / (N-1)! \prod_k \nu_k$$

Although the term $\frac{1}{2} \sum_j \nu_j$ appears as a correction to the energy, it is not related to the zero point energy as such, since it has been derived here solely as part of a more accurate geometrical method of counting the zero quantum number states. In particular this derivation makes apparent the fact that in counting levels in accordance with quantum selection rules, it is quite appropriate simply to alter the scale along one axis, and use amended values for E and ν_j in the formula

Example: It is desired only to count levels with an even quantum number for the k th. oscillator.

Here an axis m_k is substituted for the n_k axis, so that $m_k = \frac{1}{2}n_k$. Each level to be included in the count still occupies an integral lattice point. The states with odd n_k have non-integral m_k , and are simply neglected. The simplex whose contents is measured is thus

$$n_j \geq -\frac{1}{2}, \forall j \neq k; m_k \geq -\frac{1}{2}; \sum_{j \neq k} \nu_j n_j + 2\nu_k m_k < E.$$

The orthogonal edges have lengths $(E + \frac{1}{2} \sum_{j \neq k} \nu_j + \nu_k) / \nu_1$, $1 \neq k$, and $(E + \frac{1}{2} \sum_{j \neq k} \nu_j + \nu_k) / 2\nu_k$

The contents of the simplex is

$$P(E) = (E + \frac{1}{2} \sum_{j \neq k} \nu_j + \nu_k)^N / N! 2 \prod_j \nu_j$$

Similarly, in counting odd levels, one substitutes $m_k = \frac{1}{2}n_k - \frac{1}{2}$ and obtains for the contents of the appropriate simplex

$$P(E) = (E + \frac{1}{2} \sum_{j \neq k} \nu_j)^N / N! 2 \prod_j \nu_j$$

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